2011 International Nuclear Atlantic Conference - INAC 2011
Belo Horizonte,MG, Brazil, October 24-28, 2011
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: **978-85-99141-04-5**

Cluster analysis to evaluate stable chemical elements and physical-chemical parameters behavior on uranium mining waste.

Wagner de Souza Pereira[1, 2], Gustavo Ferrari de Morais[3], Delcy de Azevedo Py Júnior[1], Luis Augusto de Carvalho Bresser Dores[4], Emanuele Lazzaretti Cordova Campelo[3], Alphonse Kelecom[2] e Simone Gonçalves[1].

[1] Grupo Multidisciplinar de Radioproteção - Coordenação de Proteção Radiológica
Unidade de Tratamento de Minério - UTM, Indústrias Nucleares do Brasil - INB – MCT
Caixa Postal 961, CEP 37.701-000, Poços de Caldas Minas Gerais, Brasil
wspereira@inb.gov.br

[2] Laboratório de Radiobiologia e Radiometria Pedro Lopes dos Santos, Instituto de Biologia.
Universidade Federal Fluminense – UFF.
pereiraws@gmail.com.br or kelecom@uol.com.br

[3]Coordenação de Desenvolvimento de Processos da Unidade de Tratamento de Minério – UTM
Indústrias Nucleares do Brasil - INB – MCT
Caixa Postal 961, CEP 37.701-000, Poços de Caldas Minas Gerais, Brasil

[4]Gerência de Descomissionamento da Unidade de Tratamento de Minério –UTM
Indústrias Nucleares do Brasil - INB – MCT
Caixa Postal 961, CEP 37.701-000, Poços de Caldas Minas Gerais, Brasil

ABSTRACT

The Ore Treating Unit (UTM, in portuguese) is a deactivated uranium mine. A cluster analysis was used to evaluate the behavior of stable chemical elements and physical-chemical parameters in their effluents. The utilization of the cluster analysis proved itself effective in the assessment, allowing the identification of groups of chemical elements, physical-chemical parameters and their joint analysis (elements and parameters). As a result we may assert, based on data analysis, that there is a strong link between calcium and magnesium and between aluminum and rare-earth oxides on UTM's effluents. Sulphate was also identified as strongly linked to total and dissolved solids, and those to electrical conductivity. There were other associations, but not so strongly linked. Further gathering, to seasonal evaluation, are required in order to confirm those analysis. Additional statistical analysis (factor analysis) must be used to try to identify the origin of the identified groups on this analysis.

1. INTRODUÇÃO

Poços de Caldas Industrial Complex (in portuguese, Complexo Industrial de Poços de Caldas – CIPC) was the first brazilian uranium mining and processing unit. This facility is located in Caldas city, on Poços de Caldas plateau, Minas Gerais, Brasil. At 1996, wihtout economic viability on uranium mining activities, the CIPC was deactivated. At 2004, the CIPC received a new denomination, Ore Treatment Unit (in Portuguese, unidade de Tratamento de Minério – UTM).

The open mine pit, the waste rocks and the waste dams are sources to stable and radioactive elements, which may cause environmental impact. A waste water treatment program was created in order to minimize the environmental impact of UTM. A environmental monitoring program is kept to sustain and confirm the effectiveness of the waste treatment on mitigation of impacts and maintenance of the allowed environmental liberation limits.

Several studies on the region were made to evaluate the radiological environment impact (Impacto Radiológico Ambiental – IRA) during the plant operation [1-4]. Other authors focused the radionuclides transport on the region during the same time. Other authors focused on regional radionuclide transport during the same phase [5, 6]. Before CIPC operations, the local baseline was established by Amaral et al [7]. Brazilian laws always focused on aditional dose from radionuclides [8, 9]. Waste rock piles was studied by Fernandes [10] and Fernandes et al [11] aiming the unit's decomissioning.

This analysis was focused radionuclides liberation and dispersion to the environment. Currently environmental monitoring was given a new focus, measuring, also, stable elements liberation.

Stable and radioactive elements may cause several health problems as, for instance, neurotoxic disorders (from manganese) or renal dysfunctions (from uranium) [12]. In order to avoid those effects is necessary monitoring the heavy metals elements concentration on the effluents, to assure that those elements concentration are within the legal values. The acid mine drainage (AMD) is the most common source of water contamination by these elements in the case of mines.

AMD is a common problem and causes environmental polution [13, 14]. At UTM the waste pile rocks contains sulfides and, in the presence of water, oxigeng and bacteria iron-sulfur oxidants, produces AMD. This kind of passive leaching occurs on several mines, like a uranium mine in Salamanca, Spain, where there is also those kind of bacteria [15].

Using cluster analysis, a statistical multivariate analysis, to evaluate the behavior of the stable chemical elements and physical-chemical variables on the liquid effluents from UTM, were realized to the evaluation of physical-chemical variables (pH, electrical conductivity, oxidation-reduction potential, dissolved oxygen, total suspended solids, total dissolved solids and total solids) and of stable elements and compounds (F, Na, K, Mo, Cr, Ni, Cu, Zn, Cd, V, Ti, Y_2O_3, Mg, Al, Si, P, Ca, Mn, Fe, Ba, SO_4, TR_2O_3) on UTM's effluents. This evaluation was taken to terms with application of cluster analysis.

2. MATERIALS AND METHODS

2.1. Location

UTM locates at Caldas's city, Minas Gerais state, on Brazil. Within its limits there is a water divisor of three water bodies: Antas's stream, Soberbo's stream and Consulta's stream. UTM has three environmental interfaces, one to each water body. UTM's interface on Antas's stream is located on point 014 (Fig. 1). This point is mainly affected by the pit mine and waste pile 8 (Bota Fora 8 – BF8).

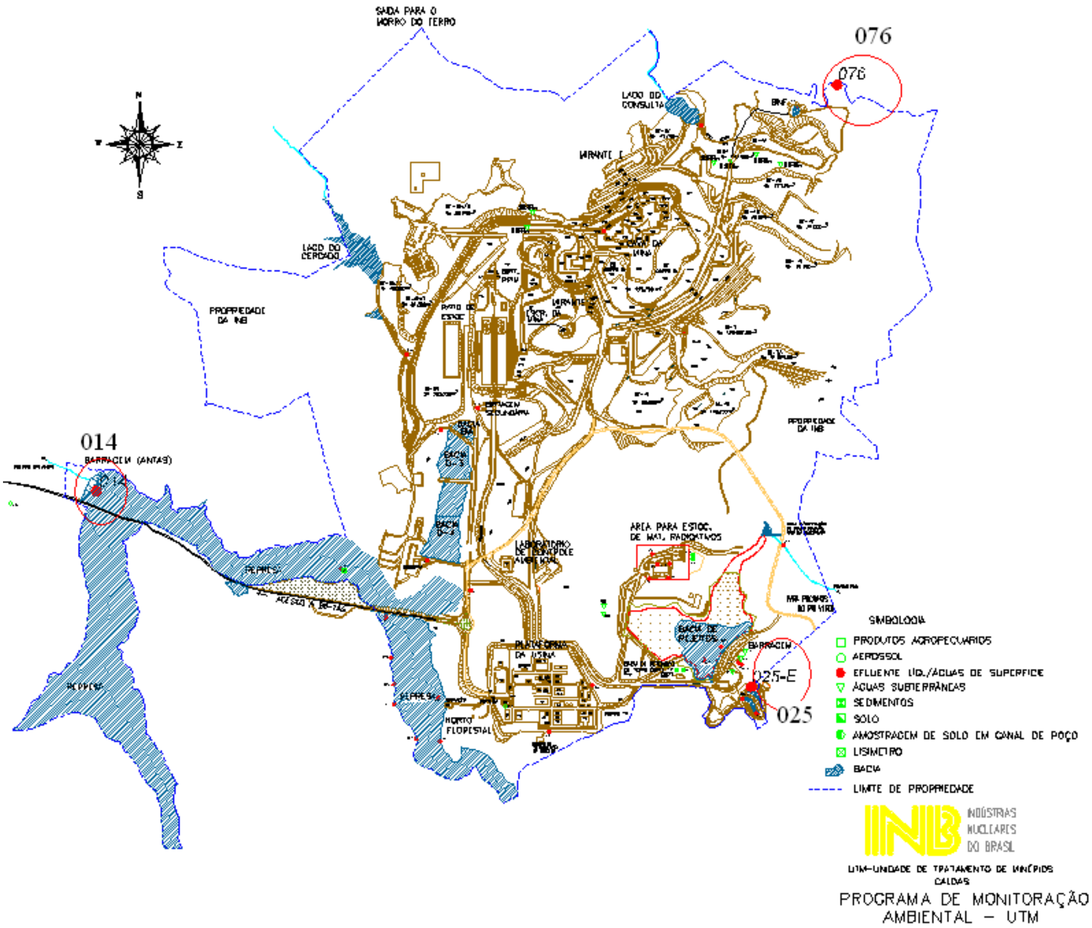

Figure 1 – Location of the study area

On Soberbo's stream the UTM interface with the environment is at point 025 (Fig. 1) mainly affected by the tailing ponds and, at last, the UTM interface with Consulta's stream is located at point 076 (Fig. 1) that is affected by the waste pile 4 (Bota Fora 4 – BF4).

2.2. Samples collection and prepare.

Samples were taken from December, 2009, to May 2010, totalizing 14 samples groups. It was used *in natura* samples to determine the physical-chemical variables [16]. Some volume was acidified (1 mL of HNO_3 to each liter of water), filtered a cellulose nitrate membrane with 0,45 μm medium porosity [16]. The filtered sample was used to measure the stable elements.

2.3. Chemical analysis of stable elements.

Fluorine was analyzed by Ion Selective Electrode [17]. Elements and compounds analysis (Mo, Cr, Ni, Cu, Zn, Cd, V, Ti, Y_2O_3, Mg, Al, Si, P, Ca, Mn, Fe, Ba, SO_4, TR_2O_3 (rare-earth oxides) was realized by ICP OES [18]. Na and K was analyzed by flame photometry. [19].

2.4. Physical-chemical analysis

pH analysis was realized according to [20], turbidity (NTU) according to [21], electrical conductivity (µS cm^{-1}) according to [22], oxidation-reduction potential (mV) according to [23], dissolved oxigen (mg L^{-1}) according to [24] and the solids (dissolved, suspended and total) in water was analysed according to [25].

2.5. Statistical analysis of clusters

Cluster analysis focus on grouping objects. This method consist on recognize some similarity, between the objects, that may unite them on the same group [26]. In this work it was used the Cluster analysis on R mode grouping objects by its descriptions [26] and [27]. As objects it will be used collected samples and as object description it will be used the values of physical-chemical and chemical analysis values. As grouping association it is used the distance realtion between those descriptors. It was used Ward's cluster grouping (minimum variance method) that is modeled by variance analysis processes [26], [27] and [28]. The method idea is to cluster the groups that minimize the square sum inside those groups, in other words, the errors square sum. As associative coefficient the distance is based on the Pearson's r coeffiecient (Pearson's 1-r) [26], [27] and [28]. Analysis was made on the statistical package Statistic, version 7.3.

3. RESULTS

3.1. Cluster analysis of stable chemical elements

All the values of concentrarion (mg L^{-1}) of Mo, Cr, Ni, Cu, Zn, Cd, V, Ti, Y_2O_3 was below the detection limits (DL), so they could not be used to this analysis. F, Na, K, Mg, Al, Si, P, Ca, Mn, Fe, Ba, SO_4, and TR_2O_3 had concentration values above the DL and it was possible to use them on the statistical analysis. The concentration of those elements may be seen on Table 1.

The results of the cluster analysis may be seen on Figure 2. On this analysis is possible to identify three groups of elements. The first one, with the lowest medium linking distance, is composed by Ca, Mg and those are associated with F. The second group is composed by SO_4, K united with Mn and P, both of them united to Na. The third group, with the highest medium linking distance between all groups identified, is composed by TR_2O_3, Al united to Si and those united to Ba and Fe. The lowest linking was found to be between Ca and Mg and between TR_2O_3 and Al.

Table 1 – Concentration values (mg L^{-1}) of analyzed elements with values above the DL.

Data	pH	F	Na	K	Mg	Al	Si	P	Ca	Mn	Fe	Ba	SO_4	TR_2O_3
		mg L^{-1}												
10/12/09	6,24	0,96	0,8	0,8	0,38	0,11	1,76	0,05	12,7	0,54	0,05	0,05	29,3	0,50
07/01/10	6,12	1,81	0,8	2,3	1,73	0,05	1,68	0,05	79,3	1,28	0,44	0,07	38,8	0,65
14/01/10	6,64	1,30	1,1	2,8	0,56	0,09	2,04	0,05	16,5	1,00	0,69	0,68	34,8	0,65
20/01/10	6,76	1,05	0,8	2,5	0,47	0,24	1,97	0,05	13,3	0,05	3,76	0,06	30,8	0,65
27/01/10	6,65	1,30	1,0	2,5	0,51	0,05	2,20	0,05	20,3	0,70	0,15	0,08	54,2	0,65
09/02/10	7,65	1,22	1,1	2,5	0,45	0,48	1,93	0,05	12,8	0,97	0,09	0,05	36,1	0,73
23/02/10	6,67	0,91	1,0	2,7	0,55	1,59	2,47	0,06	20,1	1,34	1,13	0,05	47,1	1,15
03/03/10	7,05	1,35	0,8	3,1	0,48	0,08	2,13	0,05	24,8	1,28	0,05	0,06	56,6	0,65
09/03/10	6,57	1,21	0,8	3,1	0,50	0,07	2,06	0,08	28,0	1,21	0,05	0,05	64,1	0,78
23/03/10	6,77	2,10	0,8	3,0	0,64	0,05	2,42	0,05	31,7	0,76	0,05	0,05	63,9	0,65
07/04/10	6,53	1,15	0,7	2,9	0,49	0,06	2,03	0,05	26,6	0,84	0,05	0,05	62,2	0,65
13/04/10	6,81	1,66	1,8	2,6	0,49	0,10	2,21	0,06	27,7	0,79	0,05	0,05	58,4	0,70
20/04/10	6,60	1,45	1,3	2,3	0,49	0,05	1,91	0,05	30,7	0,82	0,22	0,05	73,8	0,70
27/04/10	6,70	1,70	1,4	2,8	0,56	0,10	1,69	0,05	41,1	1,06	0,05	0,05	95,3	0,70
04/05/10	6,84	1,22	0,9	2,7	0,53	0,05	1,86	0,06	31,6	0,87	0,05	0,05	77,2	0,70

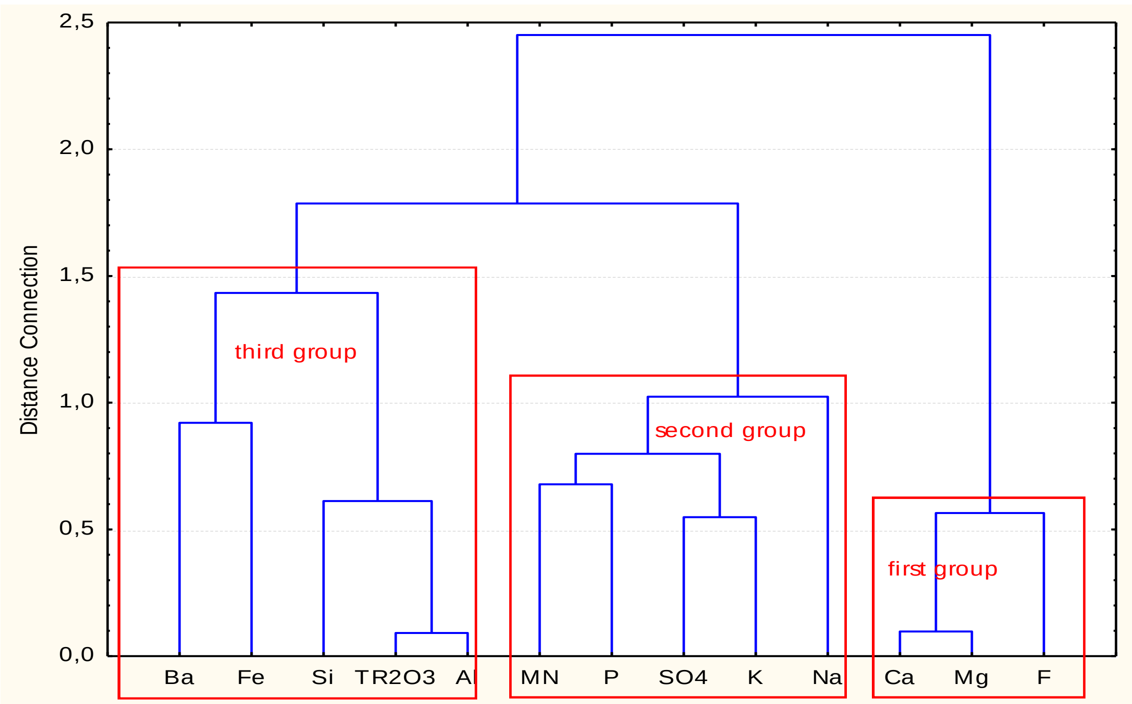

Figure 2 – Dendogram of analyzed elements, grouped by Ward's method and distances between measured points by Pearson's 1-r.

3.2. Cluster analysis of physical-chemical variables

Physical-chemical variables data, pH, turbidity (NTU), electrical conductivity – EC (µS cm^{-1}), oxidation/reduction potencial – ORP (mV), dissolved oxygen – DO (mg L^{-1}), total solids (mg L^{-1}), total suspended solids – TSS (mg L^{-1}) and total dissolved solids – TDS (mg L^{-1}) may be seen on Table 2.

Table 2 – Analysed physical-chemical variables data

Date	pH	Turbidity	Electrical conductivity	Redox pot.	OD	Total solids	TSS	TDS
		NTU	µS cm^{-1}	mV	mg L^{-1}			
10/12/09	6,24	2,0	144,7	302,5	6,46	67,5	1,5	66,0
07/01/09	6,12	4,4	122,8	291,7	7,03	74,5	15,5	59,0
14/01/10	6,64	6,5	101,6	335,9	6,13	67,5	14,5	53,0
20/01/10	6,76	5,3	89,0	329,8	6,68	71,0	16,5	54,5
27/01/10	6,65	8,0	117,1	315,9	8,06	105,0	15,0	90,0
09/02/10	7,65	5,5	112,3	337,1	6,04	93,0	15,0	78,0
23/02/10	6,67	4,6	135,1	290,7	6,52	99,0	3,0	96,0
03/03/10	7,05	3,5	162,6	222,9	6,00	129,5	10,0	119,5
09/03/10	6,57	1,8	227,0	329,7	6,53	119,5	2,0	117,5
23/03/10	6,77	4,3	173,1	478,0	6,80	115,5	1,5	114,0
07/04/10	6,53	18,0	153,5	339,8	6,21	126,5	10,0	116,5
13/04/10	6,81	4,2	182,0	300,8	7,11	142,0	9,0	133,0
20/04/10	6,60	3,1	195,6	316,9	6,71	134,0	6,0	128,0
27/04/10	6,70	2,2	290,0	298,2	6,74	192,5	5,0	187,5
04/05/10	6,84	2,5	219,0	279,3	6,52	152,5	1,0	152,5

The cluster analysis to the physical-chemical variables may be seen on Figure 3. This analysis identified three groups of variables. The first group with TDS and total solids highly linked and those two linked to EC. TSS and pH are both linked on the second group. The third group is composed by turbidity and ORP, both linked to DO.

3.3. Cluster analysis of physical-chemical parameters together with stable chemical elements.

Evaluating the stable chemical elements and the environmental variables all together the cluster analysis shows links between those variables and the elements. Sulfate is highly linked to TDS and total solids, and also to EC, as it may be seen on group 1 on Figure 4. Ba and Fe are linked between themselves and they are linked to the group og ORP and turbidity, as it may be seen on group 2, Figure 4. Si and K are linked to pH. This subgroup is linked to a group composed by Mn and P, and TR_2O_3 and Al (highly linked) linked in the same sub-group, as it may be seen on group 3, Figure 4.The last group is composed by the OD linked to Na, and this group linked to TSS, Ca and Mg are linked and this sub-group is linked to F. These two last sub-groups are linked together to form group 4, on Figure 4.

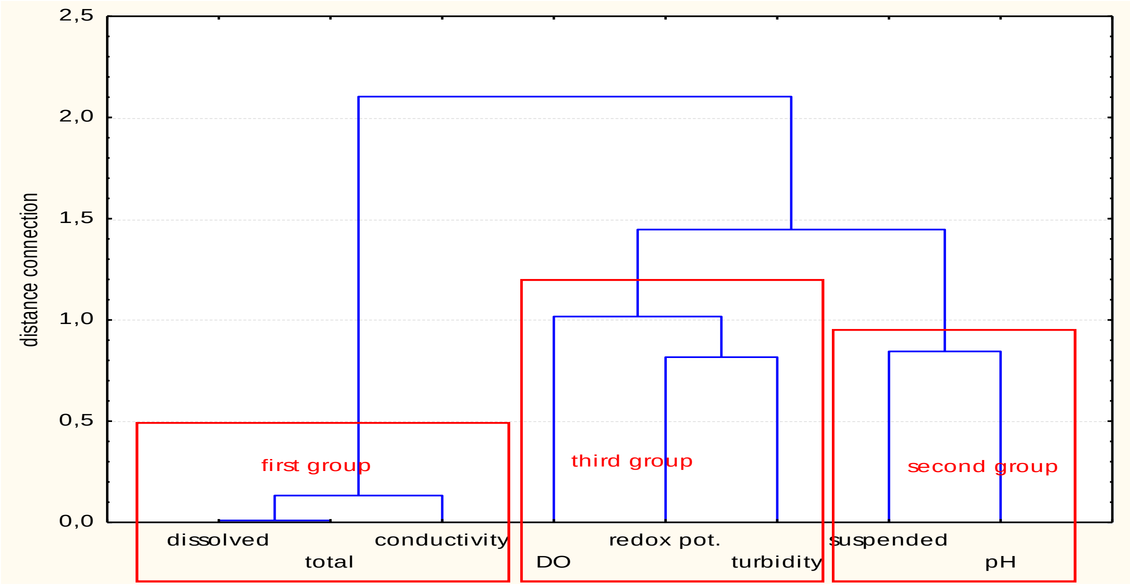

Figure 3 – Dendogram of analyzed physical-chemical variables, grouped by Ward's method and distances between measured points by Pearson's 1-r.

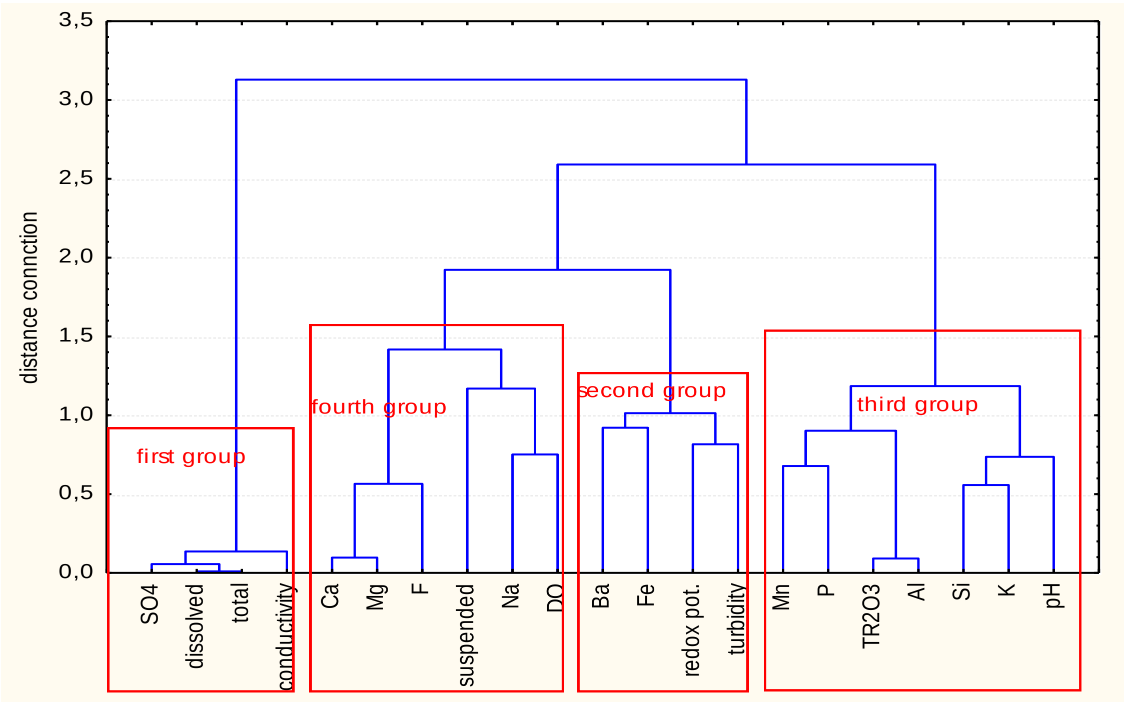

Figure 4 – Dendogram of analyzed physical-chemical variables and stable chemical elements, grouped by Ward's method and distances between measured points by Pearson's 1-r.

4. CONCLUSIONS

Cluster analysis has showed itself as an efficient tool to evaluate the association between the stable chemical elements and physical-chemical parameters that were studied in this paper.

Analyzing separately chemical elements from physical-chemical variable, followed by an analysis of the two groups together showed important because it lead to different associations between them. Analysing the physical-chemical parameters it was possible to see a link between pH and TDS. Adding the chemical elements to this analysis is possible to see that this link does not exist anymore and pH is linked to Si and K concentrations, and TDS is linked to Na and DO concentrations. Si and K has showed low links when the analysis is made only considering the chemical elements.

Sulfate is highly linked to total solids and TDS. But TSS is linked to Na and DO. Ca e Mg are highly linked, as is TR_2O_3 and Al.

The main source of chemical elements in the waste water, from point 014, is the AMD from BF4, mine pit and surroundings area. The waste water treatment plant reduces the concentration of those elements. The AMD is dependent of three main factors:water, pirite in the ore and oxygen. Seasonable variations on metal concentration are expected based on the water and oxygen availability on the rock piles, that are based on the rains of the region and the soil's water storage capability. This availability (of water and oxygen) generates fluctuations on the production of AMD, and on the characteristics of those drainages, changing the metal's source term characteristics

All the samples were taken on the raining season. Different analysis on different seasons may show different behavior on stable elements and physical-chemical variables.

Ordering analysis, other multivariate analysis technique, must be used in order to explain the associations identified on cluster analysis. Principal components analysys, factorial analysis of correspondence or discriminate analysis may be applied to this analysis.

This evaluation must be considered as a preliminary one, since there were a low sample collection and the sampling was made only on the raining season.

5. REFERERENCE

1. Fernandes, H.M., Veiga, L.H.S., Franklin, M.R., Prado, V.C.S. and Taddei, J.F. Environmental impact assessment of uranium mining and milling facilities: a study case at the Poços de Caldas uranium mining and milling site, Brazil. *Journal of Geochemical Exploration*, **52**, pp. 161-173, (1994).

2. Amaral, E.C.S. Modificação da exposição radiação natural devido a atividades agricolas e industriais numa área de radioatividade natural elevada no Brasil. Ph.D. thesis. Instituto de Biofisica, UFRJ, 130 pp. (in Portuguese). (1992).

3. Amaral, E.C.S., Godoy, J.M., Rochedo, E.R.R., Vasconcellos, L.M.H. and Pires do Rio, M.A. The environmental impact of the uranium industry: Is the waste rock a significant contributor. *Radiation Protection Dosimetry*, **22**, pp. 165-171. (1988).

4. Amaral, E.C.S., Rochedo, E.R.R., Paretzke, H.G. and Penna Franca, E. The radiological impact of the agricultural activities in an area of high natural radioactivity. *Radiation Protection Dosimetry*, **45**, pp 289-292. (1993).

5. Azevedo, H. L. P., Amaral, E. C. S. and Godoy, J. M. Evaluation of the ^{226}Ra transport by river sediments surrounding the brazilian uranium mining and milling facilities. *Environmental Pollution*, **51**, pp 259-268. (1988).

6. Barcellos, C., Amaral, E. & Rochedo, E. Radionuclide transport by Pocos de Caldas Plateau rivers, Brazil. *Environ. Technol.*, **11**, pp 533-40. (1990).

7. Amaral, E.C.S., Azevedo, H.L.P. and Mendonca, A.H. Pre-operational environment survey at the uranium mine and mill site, Poços de Caldas, Minas Gerais, Brazil. *Science of the Total Environment* **42**, pp 257-266. (1985).
8. COMISSÃO NACIONAL DE ENERGIA NUCLEAR, *Norma CNEN-NE-3.01, Diretrizes Básicas de Radioproteção*, 121 pp. (1988).
9. COMISSÃO NACIONAL DE ENERGIA NUCLEAR, *Norma CNEN-NN-3.01, Diretrizes Básicas de Proteção Radiológica*, 34 pp. (2005).
10. Fernandes, H.M., Franklin, M.R., Veiga, L.H.S., Freitas, P. and Gomiero, L.A. Management of Uranium Mill Tailings: Geochemical Processes and Radiological Risk Assessment. *Journal of Environmental Radioactivity,* **30**(l), pp 69-95. (1996).
11. Fernandes, H.M. Subsidios ao Descomissionamento da Primeira Indústria de mineração e beneficiamento de urânio no Brasil. O caso do Complexo Minero Industrial de Pocos de Caldas - Niterói. D.Sc. thesis, Departamento de Geoquímica da Universidade Federal Fluminense. 250 pp (in Portuguese). (1997).
12. Nordberg, G.F., Fowler, B. A., Nordberg, M., Friberg, L., Handbook on the toxicology of metals, Third Edition, p. 154.
13. Johnson, D.B., Hallberg K.B., Acid Mine Drainage Remediation Options: A Review, *Science of the Total Environment* **338**, pp 3-14. (2005).
14. Akcil, A., Koldas, S., Acid Mine Drainage (AMD): causes, tratment and case studies, *Journal of Cleaner Production* **14**, pp 1139-1145. (2006).
15. Mata, Y. N., González F., Ballester, A., Blásquez M. L., Muñoz J. A., Inhibition of acid rock drainage from uranium ore waste using a conventional neutralization and precipitation treatment, *Minerals Engineering* **15**, pp 1141-1150. (2002).
16. INDÚSTRIAS NUCLEARES DO BRASIL, IA-UTM-MA-04, Coleta e preparo de amostras ambientais na Unidade de Tratamento de Minério, 8 PP, (2006a)
17. INDÚSTRIAS NUCLEARES DO BRASIL, IA-UTM-CP-027, Determinação de fluoreto em águas - eletrodo seletivo, 7pp, (2007a).
18. INDÚSTRIAS NUCLEARES DO BRASIL, IA-UTM-CP-038, Matriz "AGUA" - Análise por ICP, 7pp, (2006b)
19. INDÚSTRIAS NUCLEARES DO BRASIL, IA-UTM-CP-033, Determinação de sódio e potássio por fotometria de chama, 8 pp (2004).
20. INDÚSTRIAS NUCLEARES DO BRASIL, IA-UTM-CP-031, Determinação potenciométrica de pH em águas, 10 pp, (2007b)
21. INDÚSTRIAS NUCLEARES DO BRASIL, IA-UTM-CP-032, Determinação de turbidez em águas, 7 pp, (2007c)
22. INDÚSTRIAS NUCLEARES DO BRASIL, IA-UTM-CP-041, Determinação de condutividade eletrica em águas, 8 pp, (2007d)
23. INDÚSTRIAS NUCLEARES DO BRASIL, IA-UTM-CP-068, Determinação de potencial redox, 6 pp, (2008a).
24. INDÚSTRIAS NUCLEARES DO BRASIL, IA-UTM-CP-069, Determinação de oxigênio dissolvido em água, 9 pp, (2008b).
25. INDÚSTRIAS NUCLEARES DO BRASIL, IA-UTM-CP-052, Determinação de sólidos (totais, em suspensão e dissolvidos) em água, 9 pp, (2007e).
26. Ferreira, D. F. “Estatística Multivariada”. (1 ed.). Lavras: editora da UFLA. (2008).
27. Valentin, J. L. “Ecologia numérica. Uma introdução à análise multivariada de dados ecologicos”. Rio de Janeiro: Interciência. (2000).
28. Gotelli, N. J., & Ellison, A. M. (2004). A primer of ecological statistic. sunderland: Sinauer associates. 510 pp.