CATIONS EXTRACTION OF SANDY-CLAY SOILS FROM CAVADO VALLEY, PORTUGAL, USING SODIUM SALTS SOLUTIONS

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ABSTRACT: Cases of contamination by metals in the water wells of the Cavado Valley in north-west Portugal can be attributed to the heavy leaching of clay soils due to an excess of nitrogen resulting from the intensive use of fertilisers in agricultural areas. This work focuses on the natural weathering characteristics of soils, particularly the clay material, through the study of samples collected near the River Cavado. Samples taken from various sites, after physico-chemical characterisation, were subjected to clay dissolution tests, using sodium salts of different ionic forces, to detect the relationship between certain physico-chemical parameters of water, such as pH, nitrate, chloride and sulphate content, in the dissolution of clay and the subsequent extraction of such cations as Al, Fe and K. In acidic sandy clay soils, the mineralogical composition of which was characterised by a predominance of quartz, micas, kaolinite and K-feldspars, decreases of the clay material/water pH ratio increases dissolution of the micaceous and K-feldspars phases. The presence of nitrates in the aqueous solution apparently advanced the extraction of all three cations Al, Fe and K. The specific surface area of the clay material showed a significant correlation with the main kinetic parameters of cation extraction.
Key words: nitrate, sandy clay material, natural weathering

EXTRAÇÃO DE CÁTIONS EM SOLOS ARENO-ARGILOSOS DO VALE DO CÁVADO, PORTUGAL, UTILIZANDO SOLUÇÕES DE SAIS DE SÓDIO

RESUMO: Têm ocorrido casos de contaminações de águas de poços, por metais, no vale do Rio Cávado, região noroeste de Portugal. A princípio, poderiam ser explicáveis pela elevada lixiviação dos solos areno-argilosos da região, quando da prática de adubações intensivas de nitrogênio em áreas agrícolas. Assim, estudaram-se as características do intemperismo natural dos solos, particularmente da fração argila, característica da margem norte do rio Cávado. Coletaram-se amostras de vários locais, que foram submetidas, após caracterização físico-química, a ensaios de dissolução a partir de soluções de sais de sódio com diferentes forças iônicas. O objetivo foi observar as relações de determinados parâmetros físico-químicos da água, tais como: pH, nitratos, cloretos e sulfatos na dissolução das argilas e a conseqüente extração de espécies químicas tais como Al, K e Fe. Para solos areno-argilosos, ácidos, cuja composição mineralógica se caracteriza por um predomínio de quartzo, micas, caulinita e feldspato-K, o abaixamento do pH da suspensão solo/água promove a solubilização das fases micáceas e feldspáticas. A presença do nitrato nas soluções aquosas promoveu aparentemente a extração de todos os três cátions: Al, K e Fe. O efeito da área superfícial específica das partículas dos solos condicionou fortemente vários dos parâmetros cinéticos estudados relativos à extração dos cátions.
Palavras-chave: nitrato, material areno-argiloso, intemperismo natural

INTRODUCTION

The natural weathering of soils constitutes an important geological process for humans, since it promotes soils genesis and contributes to the formation of economically important mineral deposits such as kaolinite, laterite, bauxite, bentonite, charcoal and petroleum (Gomes, 1988). However, this is a complex phenomenon, of interdisciplinary understanding, covering knowledge of several areas such as pedology, hydrology, biology, geochemistry and physics. Water, an important constituent of soil is the most relevant agent in weathering. The percolation of water, with its content of gases and organic and inorganic ions, is the driving force for reactions, prior to its arrival at groundwater.

In the last twenty years important advances have occurred in the understanding of the hydrogeochemistry of soil/water systems. Studies on the weathering mechanisms that occur in shallow soils have been undertaken in response to the need for analysing pollution impact caused from agricultural practices on the subsurface horizons and the effects of acid precipitation in highland areas. In environments of greater depth, research into the development of geothermal energy and the deposition of radioactive wastes has produced an extensive database. Despite these advances, the perception of measures, quantifying and the modelling atmospheric water flow, through soil vegetation in satured and unsatured zones, is still in a relatively early stage of development (Saether & Caritat, 1997). Therefore it is imperative to develop parameters for the elucidation and

prediction of models aiming at understanding the phenomena that occur in the soil complex.

The contamination by metals of water wells in the region under study can be explained by heavy leaching of clay soils by the intensive application of nitrogenous fertilizers (TecMinho, 1998). Lack of control over the practice of soil fertilization has been constant preoccupation by the member states of the European Union, who, by means of community law, such as the Council Directive 91/676/CEE, enacted in Portuguese legislation by D.L. N° 235/97 3rd September, recommending to member states the creation and application of one or more codes of good agricultural practice, setting out techniques and standards relating to the use of this kind of fertilizer with the objective of lowering or eliminating contamination of surface and ground water. These orientations and directives for managing nitrogen in agricultural ecosystems were published in the "Códigos de boas práticas agrícolas para a protecção da água contra a poluição com nitratos de origem agrícola", the official document of the Portuguese Ministry of Agriculture (1997).

MATERIAL AND METHODS

Collection and Characterisation of samples

Soil Samples were collected at depth of about 50 cm on the north margin of the River Cavado, in north-west Portugal, in non-agricultural areas of different points bordering between the localities of Amares and Barcelos (Figure 1). Resorting to geological charts and soil and climate maps it was observed that this is a region of podzolic soils, a moist-temperate climate where the mean precipitation (2000 mm year^{-1}) is higher than evapotranspiration (800 mm year^{-1}). Extensive deposits of biotitic and muscovitic granite were identified, with biotitic predominating. The chemical composition of samples collected (Table 1) was determined by X rays fluorescence spectrometry – XRF with an "X Unique II - Philips" device. Each sample was prepared for analysis using the following procedure: (a) about 10 g of each sample was dried at 105°C during 24 h; (b) the sample was ground it in ball mill (recipient and balls made of alumina), during 20 min. obtaining particles size < 0,6 mm; (c) 4 g of mixture (3,2 g milled sample + 0,8 g
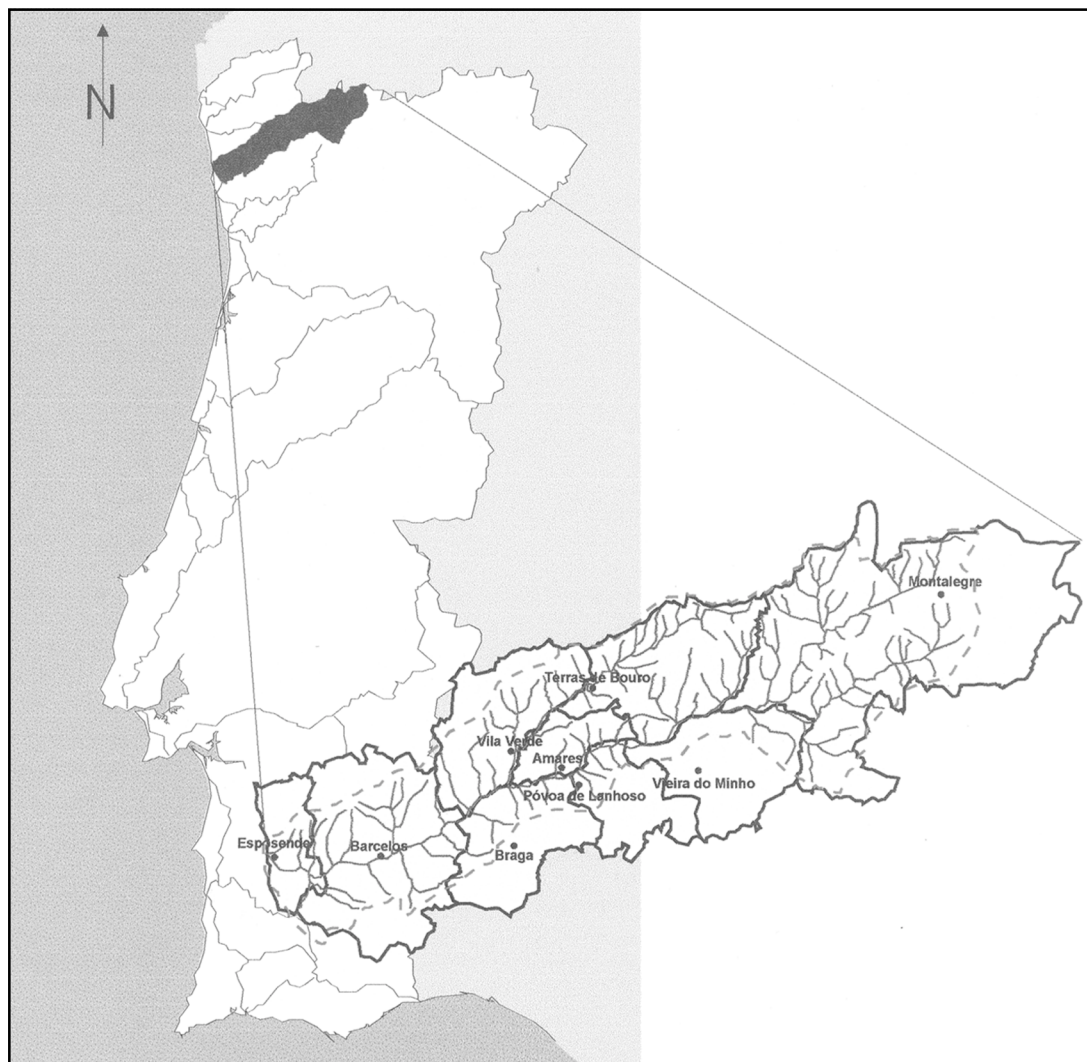

Figure 1 - Hydrological Basin of the River Cavado. Geographic location of the region where the samples were collected. Map elaborated by Regional Board for the Environment – Portuguese Ministry of the Environment.

agglutinant resin) was weighed and pressed, forming a pastille, 30 mm in diameter. Standard curves were established with reference materials (clays and others minerals) certified by international organisms for the XRF analysis to which the pastille was submitted. The pH values of soil-water suspension (pH_{susp}) to a 1:10 ratio were determined (Table 1). The specific surface area (SA) of samples (Table 1) was measured by equipment "Gemini II 2370" using the BET method (Brunauer, Emmet and Teller, 1938). Samples in powder were submitted to X rays diffraction – XRD using device "Rigaku". The qualitative presence of quartz, kaolinite, magnesian muscovite and K-feldspar was detected.

Grouping of samples

The values presented on the Table 1 were submitted to statistical treatment and those can be grouped into samples in accordance to the similarity in their chemical composition. The methodology used (Castro et al., 1997) obeyed the following procedure: a) determination, for each oxide or element, the mean and the respective standard deviation; b) calculation of euclidian distance, allowing a first sorting among samples to be realized; c) creation of groups, using the method "Nearest Neighbour" based on the Hotelling multivariate analysis (1933), that has as its criterion the aggregation or not of a determined sample into a pre-formed group. A minimum level of probability of 95% was established (Castro et al., 1997).

Taking into account the pre-established conditions, samples were grouped as presented on the Table 2. Based on this grouping the samples were submitted to a descriptive statistic analysis (Table 2), with means, standard deviations and errors, total and for each group of samples.

Dissolution/extraction tests

The dissolution of soil samples experiments for cation extraction occurred with slight adaptations to protocol DIN 38414-S4 (1984). This norm defines a method for determining leaching in solids using water and it has been regularly applied as a test for evaluating ecotoxicity for the purposes establishing suitability for landfill. Instead of using water as the extraction solution, aqueous solutions of sodium salts were made, characterized by higher ionic forces, as described below. For this stage one sample of each group was taken, that is, samples 2, 9, 15 e 18 were selected. The solutions were prepared using the following salts and respective concentrations: anhydrous sodium nitrate -150 mg L^{-1}, anhydrous sodium chloride -1000 mgL^{-1}, anhydrous sodium sulphate -1000 mg L^{-1} and their combinations, in addition to the blank (just distilled water). Such values were chosen since they represent the orders of magnitude of concentration of the respective ions present in the groundwater of the region under study (TecMinho, 1998). The solutions started with initial pH values: 4,5, 6 and 7, using acid of the same ionic group or NaOH.

The procedure, contained in the protocol mentioned previously, consisted of drying of material at 105°C during 24 h. 80 g of material and 800 mL of solution (1:10 solid/liquid ratio) were utilized and the mixture was kept in hermetically sealed 1000 mL plastic flasks. The bottle containing the mixture was placed in the dissolution

Table 1 - Values of pH ($pH_{susp.}$), specific surface area (SA) and chemical characterisation of samples of clay material.

Sample	$pH_{susp.}$	SA	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	TiO_2	CaO	MgO	Ba	Zr	Sr	Rb	Mn
	1:10	$m^2 g^{-1}$	—— $g kg^{-1}$ ——						
1	6.9	2.8	624	215	55	51	12	11	11	20	0.87	0.35	0.17	0.26	0.70
2	7.0	21.8	561	286	76	38	2	15	3	17	0.98	0.35	0.13	0.31	0.50
3	7.3	12.1	580	247	81	36	4	16	4	28	1.40	0.50	0.13	0.22	0.59
4	8.1	18.6	571	267	76	40	3	15	4	23	0.91	0.46	0.10	0.28	0.48
5	6.5	10.5	538	254	122	48	4	13	1	18	0.91	0.37	0.06	0.27	0.58
6	5.3	9.4	531	321	94	34	0	13	0	6	0.51	0.52	0.08	0.20	1.02
7	5.0	17.5	474	358	81	56	0	14	0	14	1.19	0.53	0.17	0.33	0.52
8	5.2	12.3	559	298	81	37	0	13	0	9	0.63	0.36	0.04	0.25	0.82
9	5.0	9.8	528	331	110	10	2	15	0	1	0.71	0.42	0.01	0.06	1.52
10	5.2	7.2	569	284	75	31	0	12	0	27	0.31	0.36	0.01	0.13	0.86
11	5.3	11.7	568	309	79	25	0	13	1	4	0.86	0.38	0.04	0.06	0.31
12	4.9	17.7	528	331	110	10	2	15	0	1	0.71	0.42	0.01	0.06	1.52
13	4.8	38.0	534	340	78	22	0	18	0	6	0.50	0.31	0.04	0.20	0.29
14	7.9	5.0	621	216	57	51	8	15	6	22	1.50	0.41	0.18	0.24	0.60
15	5.3	5.3	546	289	125	17	2	14	0	5	0.48	0.25	0.01	0.08	0.43
16	5.0	8.7	515	346	65	50	0	11	0	11	1.16	0.49	0.10	0.31	0.36
17	5.4	7.6	488	322	89	46	9	14	8	20	1.32	0.59	0.22	0.40	0.74
18	5.0	9.0	532	306	77	48	2	13	2	18	1.28	0.49	0.18	0.36	0.51
19	5.4	4.0	510	336	68	50	4	11	4	14	1.37	0.52	0.24	0.36	0.69
20	4.9	18.1	520	270	148	31	3	13	1	12	0.57	0.26	0.02	0.14	0.46
21	5.6	10.7	400	283	288	10	2	12	1	3	0.15	0.26	0.07	0.09	0.60
22	5.8	6.5	472	332	167	11	3	11	2	2	0.25	0.36	0.25	0.07	0.37

Table 2 - Descriptive statistical analysis of pH values ($pH_{susp.}$), specific surface area (SA) and chemical composition of samples.

		pH_{susp}	SA	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	TiO_2	CaO	MgO	Ba	Zr	Sr	Rb	Mn
all the samples	x	5.76	12	535	297	100	34	3	14	2	13	0.84	0.41	0.10	0.21	0.66
	DP	1.02	7.77	49	41	51	15	3	0	2	8	0.40	0.10	0.08	0.11	0.33
	s	0.22	1.66	11	9	11	3	1	0	0	2	0.08	0.02	0.02	0.02	0.07
Group 1 samples 8,11,15,20	x	5.17	11.85	548	292	108	28	2	13	0	7	0.64	0.31	0.03	0.13	0.51
	DP	0.19	5.27	17	14	33	10	0	0	0	6	0.16	0.07	0.02	0.09	0.22
	s	0.09	2.63	9	7	17	5	0	0	0	3	0.08	0.03	0.01	0.04	0.11
Group 2 samles 6,9,12	x	5.07	12.33	529	328	105	18	1	14	0	3	0,64	0,45	0,03	0,11	1.35
	DP	0.21	4.69	7	10	12	14	1	0	0	0	0,12	0,06	0,04	0,08	0.29
	s	0.12	2.71	4	6	7	8	0	0	0	0	0,07	0,03	0,02	0,05	0.17
Group 3 samples 7,16,18,19	x	5.10	9.77	508	337	73	51	1	12	2	14	1.25	0.51	0.17	0.34	0.52
	DP	0.2	5.59	26	22	10	10	1	0	0	0	0.09	0.02	0.06	0.02	0.13
	s	0.1	2.79	13	11	5	5	0	0	0	0	0.05	0.01	0.03	0.01	0.07
Group 4 samples 2,3,4,5	x	7.22	15.73	563	264	89	41	3	15	3	21	1.05	0.42	0.11	0.27	0.54
	DP	0.67	5.35	22	17	24	8	0	0	0	8	0.24	0.07	0.03	0.04	0.06
	s	0.33	2.68	11	9	12	4	0	0	0	4	0.12	0.04	0.02	0.02	0.03
Group 5 samples 1,14	x	7.4	3.87	623	216	56	51	10	13	8	21	1.19	0.38	0.18	0.25	0.65
	DP	0.71	1.58	0	0	0	0	10	0	10	10	0.45	0.04	0.01	0.01	0.07
	s	0.5	1.11	0	0	0	0	0	0	7	7	0.32	0.03	0.01	0.01	0.05

x – mean; DP – standard deviation; s – standard error

apparatus, both phases to be in permanent contact during 24 h., turning at a rate of 0,5 rotation/min. Afterwards the solution was filtered in "Rundfilter" MN 1674 paper and the filtrate was centrifuged at 6000 rpm during 1 h.

The K content was determined from the extract using atomic absorption spectrometry –flame emission, in the "GBC" model 904 AA, apparatus and the contents of Al and Fe by Colorimetry, that is, the Al by Eriochrome Cyanine R method in alkaline medium, and Fe by 1,10-Phenantroline method. Both determinations were carried out in "Hanna Instruments" equipments (Standard Methods, 1992).

Data analysis

In a preliminary statistical analysis, Pearson's Correlation Coefficient – PCC was determined for each pair of variables, providing a quantitative adimensional measure of the power of the linear relationship between two variables, varying between - 1 and 1 (Mendenhall & Sincich, 1995). Significance level of 5% was used to determine whether the correlations were significant from a statistical viewpoint. If the relationships could be established describing significative effects among the variables, a multiple regression analysis was performed. For each equation the power of the regression was calculated – PST and it was taken as a critical measure of the sensitivity in the hypothesis testing. For the treatment of data NCSS (2000) software was used the. Also the r^2, which is the coefficient of determination, was calculated for each case. A significance level of 5% was employed.

RESULTS AND DISCUSSION

Total chemical composition of materials

In the chemical analysis (Table 1) the percentage in Al_2O_3 (overall mean of 297 g kg^{-1}) was shown to be relatively high, higher than that (160 g kg^{-1}) found in literature for the region under study (Vieira e Silva, 1980; Braga, 1986). This may indicate a more significant current presence of kaolinite, which could be the result of the weathering process, occurring over the years in this region. The presence of K_2O is intimately associated to compounds CaO, MgO, Ba, Zr, Sr and Rb, but mainly MgO, Ba and Rb, a fact justified by the values of CCP correlation obtained; all CCP values above 0,85 between K_2O and other constituents being indicative of the presence of micas. The mean contents of K_2O, Na_2O, CaO, MgO, Ba, Sr and Rb, when compared to respective overall averages (cf. Table 2) are relatively low for samples in groups 1 and 2, and high for groups 3, 4 and 5. In the latter groups the contents of Ba and Sr probably corresponds to the presence of K-feldspar, whereas the other constituents show concentrations related to micas.

The molecular ratio of SiO_2/Al_2O_3, or Ki value, is used as a criterion for discriminate the phases present in the clay fraction (Harrassovitz, 1926 – mentioned by Aoudjit et al., 1996). In this case, the Ki mean value is 3,06, which suggests a significant presence of clay minerals of type 2:1, such as smectites and/or

vermiculites, as well as micas, cited previously. These clay minerals have their genesis in the transformation of biotite, that is the predominant phase of granitic deposits where the samples were collected (Burkins et al., 1999).

"pH of soil" (pH$_{susp}$)

Two types of very distinct pH suspension values (pH$_{susp}$) were observed. The first type constitutes the samples 1, 2, 3, 4, 5 and 14 belonging to groups 4 e 5, with mean pH$_{susp}$ of 7,3. The others 16 samples show a mean pH$_{susp}$ of 5,2. Comparing the higher pH$_{susp}$ values of the samples groups 4 and 5 and the others groups, whose pH$_{susp}$ values are lower, with the contents of K_2O, Na_2O, CaO, MgO, Ba, Zr, Sr and Rb, a direct relationship between the magnitude of pH and mean content values of the previously mentioned constituents can be observed. The samples group with high mean pH$_{susp}$ values corresponds to samples group with high mean contents of those constituents, when compared to overall mean. Correlating all pertinent parameters, the following expression for the pH suspension could be estimated:

$$pH_{susp} = 10,7 + 3,3.10^{-2}(SA) - 0,23(Al_2O_3) + 3,6. \ 10^{-3}(Sr) + 2,6. \ 10^{-3}(Zr) \ (r^2 = 0,74) \quad [1]$$

In both K-feldspar, micas and others clays 2:1 type minerals, in which is usual to detect the mentioned compounds (K_2O, Na_2O, CaO, MgO, Ba, Zr, Sr e Rb), the lowering of medium pH promotes the weathering process by the action of the present acidity, as well as the contribution from plants roots, which release H^+ and absorb K and silica, accelerating the process of alteration of these minerals with consequent release of K from their structure (Aoudjit et al., 1996; Burkins et al., 1999; Priscia et al. 1999). Therefore, it is possible to relate samples relatively richer in micaceous and feldspars phases (represented in expression [1] by higher concentrations of elements Zr and Sr) to samples with higher pH$_{susp}$ values, whereas samples richer in the kaolinitic phase (represented in expression [1] by the higher content in Al_2O_3) to samples with more acidic pH values.

Specific surface area (SA)

A relationship between the contents of TiO_2 and the specific surface area values (SA) was detected, which is:

$$SA = -29,10 + 30,28(TiO_2) \ (r^2 = 0,47) \quad [2]$$

Aoudjit et al. (1996) cited that for all soils the presence of biotite is associated to the Ti presence, and the geological context of most of the points where the samples were collected shows the presence of granite of two micas: biotitic and muscovitic. This leads us to believe there is some relationship between these facts. On the other hand, Gomes (1988) cites that in raw kaolin, a clay material rich in kaolinite, the variation of TiO_2 contents, present in the anatase and biotite phases, is inversely related to material granulometry, through its concentration in thinner fractions. Therefore it is directly associated to its specific surface area, which is in accordance with the relationship obtained in expression [2].

Dissolution/extraction tests

By cross referencing all information related to the extraction of metal chemical species obtained through the dissolution of samples with the variables evaluated in the tests, the following expressions could be obtained:

$$Al = 0,89 + 0,12 \ (Rb) + 1,70 \ (Na^+) - 0,34 \ (pH_{susp}) + 6,9.10^{-2} \ (SA) \ (r^2 = 0,73) \quad [3]$$

$$K = -8,52 + 0,97 \ (MgO) + 1,38 \ (Na^+) + 1,73 \ (pH_{susp}) + 0,13 \ (SA) \ (r^2 = 0,71) \quad [4]$$

$$Fe = -2,99 + 1,34 \ (CaO) + 3,01(Na^+) - 0,67 \ (pH_{susp}) \ (r^2 = 0,32) \quad [5]$$

In these experiments, solutions of sodium salts, with higher concentrations than the soil solutions, were used. As was observed by Barrow (1999) and Sposito (1989) the increase of the concentration of salts cause the reduction of the absolute value of the electric potential next to the loaded surface of the mineral phase. If the potential is negative, as it is the case of the clay minerals phases of type 2:1, it becomes less negative. It is believed that the decrease of the negative character of the surface can not only facilitate the adsorption of anions with affinity to it, but can also promote the release of cations adsorbed in the mineral surface. Barrow and Sposito further cite that the increase of salts concentration supposedly used to remove exchangeable ions can remove metal ions covalently adsorbed. Bertsch and Seaman (1999) report in their work that diluted sodium solutions had been inefficacious in dislocating exchangeable native cations associated with phyllosilicates minerals, while upon increasing the concentration of the sodium solutions, these native cations, including Al, had been dislocated. Based on these estimates and references and in the concentration values of extracted cations, it is probable that weathering has occurred. An analysis of the effect of the evaluated parameters follows.

The effect of the chemical composition of micaceous minerals, represented by the content of Rb and of the component related to the phenomenon of ionic exchange, which is the presence of cation Na^+, have weights relatively little significance in relation to other terms in the expression [3]. While for the effects of the specific surface area and pH suspension PST values of 99% were obtained, the effect of the Rb content in the soil produced a value of 71% and the presence of the Na^+ a 35% value. This suggests a lesser certainty in affirming the influence of the chemical composition and of the ionic exchange by Na^+ as the process that controls Al cation extraction, in accordance with the equation proposed above. However it is known that, in acidic soil,

the most important metal cation readily exchangeable is the Al^{3+} (Turpault et al., 1997, Sposito, 1989). Given that the Rb constituent represents the composition of micas, this affirmation is explained by the values of Pearson´s coefficients of correlation - CCP between this element and the main constituent of the micas present in the clay material, which are all close to 0.90. The term relating to pH_{susp} in expressions [3] and [5], being negative in value, tend to confirm that the transformations of primary minerals, of the micas and clay minerals of type 2:1 occur with a lowering of pH in soils developed from granitic deposits (McGahan et al., 1998, Aoudjit et al., 1996). Regarding the specific surface area (SA), it is possible to conclude that the reactions occurring in the soil will be more effective, the greater the SA of the mineral phase that is exposed to weathering (Coutinho, 1989).

In accordance with expression [4], the chemical composition influences the solubilization of the K, through the presence of mica phases, clay minerals of the type 2:1 and K-feldspar. Effectively a PST of 91% was obtained for the MgO. The process that controls the extraction of cation K has a contribution relatively more significant contribution, through a PST equal to 68%. It is probable that cationic exchange has occurred between the exchangeable K of the feldspar, or of the smectite surface, and the Na, that in this in case, would perform as the indice ion (Sposito, 1989). The effects of SA and pH_{susp}. still influence more strongly the extraction of the K, since that the powers of the statistical test (PST values) for both the terms presented values close to 100%.

In equation [5] the obtained relationship presents a low r^2, indicating only a small part of the variability was explained by the variables used. However, it can be concluded that that value of r^2 is statistically significant taking in account the number of assays carried out. The terms relating to the chemical composition and to the process that controls the extraction of cation Fe indicate, in a less significant way, the effects of the variables CaO and Na^+, presenting PST values equal 81% and 50% respectively, against PST of 100% for pH_{susp}.

In this stage of the analysed extraction of cations, no significant influence of the action of anions NO^-_3, SO^{2-}_4 and Cl^- was registered.

Grouping of results of metal cation extraction in accordance with the test conditions

The results were submitted to descriptive statistical analysis, ordering the samples according to groups of chemical analysis, test conditions of cation extraction solutions and the initial pH of the test (cf. Table 3). It was possible to observe that group 4 was the one where the most significant extraction of all three cations had occurred. Group 4 is formed by samples 2, 3, 4 and 5, that are distinguished by being apparently rich in micas and other minerals of type 2:1 and containing some K-feldspar.

Solutions only containing nitrate (without the addition of sulphate nor chloride) extracted more Al than solutions that did not contain this ion, with an average of Al = 0.63 mg L^{-1}. However, given the great variability of the results, the obtained difference was not strongly significant. K was more strongly extracted in solutions only containing nitrate+chloride (no sulphate addition), with mean of K = 3.20 mg L^{-1}, although this effect also is not statistically significant. The Fe was more strongly extracted in solutions only containing nitrate (no addition of sulphate nor chloride), with mean of 1.23 Fe = mg L^{-1}, though also in this case, the effect is not statistically significant.

The nitrate proved to be, amongst all the solutions tested, the accompanying anion whose presence coincided with the highest levels of cation extraction analysed; sometimes alone as in the cases of the Al and Fe, other times associated to anion chloride anions, as in the case of the K; which was as had been foreseen. It is known that nitrate and chloride anions, in aqueous solution with the same effective ionic diameters (3Å - Kielland, 1937) can have similar behaviour upon forming internal sphere complexes, can have similar behaviours. However these complexes has difference of the behaviour of complexes of inter. However these complexes have behavioural differences to the complexes of internal sphere formed from bivalent ions, when in solution, as in the case of sulphate, which, upon reacting form a bidentate binding to the surface adsorbent (Barrow, 1999, Garrels and Christ, 1965). The

Table 3 - Grouping of results of cation extraction.

Grouping	Nr. Tests	Al	K	Fe
			Mean Values	
		-------- mg L^{-1} ---------		
pH				
4,5	60	0.48	2.23	0.52
6	60	0.29	2.74	0.19
7	60	0.28	2.83	0.45
Extraction solution				
NO^-_3	20	0.63	2.87	1.23
SO_4^{-2}	20	0.26	2.38	0.10
Cl^-	20	0.48	2.59	0.20
$NO^-_3 + SO_4^{-2}$	20	0.10	2.85	0.16
$NO^-_3 + Cl^-$	20	0.46	3.20	0.13
$SO_4^{-2} + Cl^-$	20	0.29	3.13	0.04
$NO^-_3 + SO_4^{-2} + Cl^-$	20	0.27	2.63	0.06
Group				
1	35	0.26	1.00	0.08
2	35	0.07	1.91	0.06
3	35	0.47	1.51	0.17
4	35	0.47	6.38	1.20

relationship between the presence of nitrate and the extraction of Al is in accordance with Turpault et al. (1997) who, upon analysing the extracts of leaching experiences on samples collected in acidic soil over a period of 20 months, observed that the mobilization of the Al was directly associated to the presence of nitrate in the water. The higher extractions for Al and Fe had occurred for pH 4.5, with mean values of 0.48 mg L^{-1} and 0.52 mg L^{-1}, respectively. Acidic environments determine a higher mobility of metals, such as Al and Fe, when they undergo hydrolysis reactions (Bertsch, 1999). The pH 7 was responsible for the higher extractions of the K, with mean concentration of 2.83 mg L^{-1}, which can be explained by the ionic exchange between the K of K-feldspar, whose primary mineral phase is accessible to this pH, and the Na, derived from salts. As was observed by Barrow (1999), in the sorption process, a rise of pH increases the effect of monovalent ions, as in the case the Na^+.

CONCLUSION

The parameters that most markedly affect the extraction of chemical species under study are the pH values of soil/water suspension and the specific surface area.

Although the statistical analysis does not allow an unequivocal correlation between the presence of anions and the dissolution of the clay material, the higher values that were obtained with the solutions containing nitrate seem to evidence some effect of this anion in the complex process of chemical equilibrium. The understanding of the behaviour of nitrates and their relationship with the metal chemical species conveyed in the soil complex, which can be solubilized at contamination levels, compromising the ecosystem, require an exhaustive knowledge of the soil and its evolution.

With regard to nitrogen fertilization practices, its specific behavior in the soil impose that the fertilization with this nutrient, along with the crop techniques used that may influence its dynamics, are managed in such a way as to limit to the maximum degree its transport through drainage waters, thereby reducing the risk of contamination from nitrates and metal chemical species in the aquatic systems.

REFERENCES

AOUDJIT, H.; ELSASS, F.; RIGHI, D.; ROBERT, M. Mica weathering in acid soils by analytical electron microscopy. **Clays Minerals**, v.31, p.319-332, 1996.

BARROW, N.J. The four laws of soil chemistry: the Leeper lecture 1998. **Australian Journal of Soil Research**, v.37, p.787-929, 1999.

BERTSCH, P.M.; SEAMAN, J.C. Characterization of complex mineral assemblages: Implications for contaminant transport and environmental remediation. **Proceedings of the National Academy of Sciences of the USA**, v.96, p.3350-3357, 1999.

BRAGA, M.A.S. Gibsite em estruturas filonianas e em perfis de meteorização de rochas graníticas do Minho. In: CONGRESSO NACIONAL DE GEOLOGIA, 1., Lisboa, 1986. **Boletim**. Lisboa: Sociedade Geológica de Portugal, 1986. p.7-16.

BRUNAUER, S.; EMMET, P.H.; TELLER, E. Adsorption of gases in multimolecular layers. **Journal American Chemical Society**, v.60, p.309-319, 1938.

BURKINS, D.L.; BLUM, J.D.; BROWN, K.; REYNOLDS, R.C.; EREL, Y. Chemistry and mineralogy of a granitic, glacial soil chronosequence, Sierra Nevada Mountains, California. **Chemical Geology,** v.162, p.1-14, 1999.

CASTRO, F.; OLIVEIRA, P.; FERNANDES, I.M. Development of a methodology for the estimation of the provenance of archaeological, ceramics. In: METHOD AND THEORY IN HISTORICAL ARCHAEOLOGY, "MEDIEVAL EUROPE BRUGGE 1997" CONFERENCE ZELIK, Zelik, 1997. Guy de Boe & Frans Verhaeghe, 1997. p.123-128.

COUTINHO, J.F. Acidez do solo e toxicidade do alumínio: calibração de métodos de avaliação da necessidade em cal. Vila Real, 1989. 709p. Tese (Doutorado) - Universidade de Trás-os-Montes e Alto Douro.

GARRELS, R.M.; CHRIST, C.L. **Solutions, minerals, and equilibria.** New York: Harper and Row, 1965.

GOMES, C.F. **Argilas:** o que são e para que servem. Lisboa: Fundação Calouste Gulbenkian, 1988. 457p.

HOTELLING, H. Analysis of a complex of statistical variables into principal components. **Journal of Education Psychology**, v.24, p.417-441, 489-520, 1933.

KIELLAND, J. Individual activity of ions in aqueous solutions. **Journal of American Chemical Society**, v.59, p.1675-1678, 1937.

MCGAHN, D.G.; ZASOSKI, R.J.; SOUTHARD, R.J. **Bulk and Rhizosphere pH as indicators of soil quality:** A comparison of agriculturally-acidified and naturally-ocurrency acid soils. 1997-1998 Project Summary. California, USA, Kearney Foundation of Soil Science, Division of Agricultural and Natural Resources. University of California. 1998.

MENDENHALL, W.; SINCICH, T. **Statistics for engineering and the sciences**. 4.ed. New Jersey: Prentice-Hall, 1995. 561p.

MINISTÉRIO DA AGRICULTURA DE PORTUGAL. **Códigos de boas práticas agrícolas para a protecção da água contra a poluição com nitratos de origem agrícola**. Lisboa: MADRP, 1997.

NUMBER CRUMCHER STATISTICAL SYSTEM - NCSS. **Statistical analysis & data analysis software**. Kaysville, 2000.

PRISCIA, O.; JERÔME, V.; BERNARD, D.; JEAN, P.F.; FRANÇOIS, M.; JEAN J.B.; DANIEL, N.; HENRI R. The effect of organic matter on chemical weathering: Study of a small tropical watershed: Nsimi - Zoételé site, Cameroon. **Geochimica et Cosmochimica Acta**, v.63, p.4013-4035, 1999.

SAETHER, O.M.; CARITAT, P. (Ed.) **Weathering and groundwater recharge in catchments**. Rotterdam: A.A. Balkema Brooksfield, 1997. cap.129, p.5-10: Geochemical processes (Geological Survey of Norway).

SPOSITO, G. **Chemical equilibria and kinetics in soils**. New York: Oxford University Press, 1994. 277p.

SPOSITO, G. **The chemistry of soils**. New York: Oxford University Press, 1989, 278p.

Standard methods for the examination of water and waste water. 18.ed. Washington: APHA, 1992. p.3-44, 3-66.

TECMINHO – ASSOCIAÇÃO UNIVERSIDADE – EMPRESA PARA O DESENVOLVIMENTO. **Avaliação da eventual responsabilidade da empresa Alumínios Ibérica Ltda na contaminação de poços da Freguesia de Lago, Concelho de Amares.** Braga, Portugal, 1998.

TURPAULT, M.P.; PONETTE, Q.; BELKACEM, S.; NYS, C. Clay transformations following a leaching experiment on an acid brown soil. **Clays Minerals,** v.32, p.289-297, 1997.

VIEIRA e SILVA, J.M. Ocorrência de vermiculite-Al e gibsite em solos de granito do Noroeste de Portugal. Génese destes minerais. **Serviços de Geologia de Portugal**, v.66, p.71-77, 1980.