

SEASONAL VARIATIONS ON SYSTEMS OF TRIPLE INFLUENCE

The Importance of Silicate Weathering, Soil Fertilization and Domestic Effluents to the Composition of Stream Water as Determined by Correspondence Analysis

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Abstract

The chemical composition of stream waters from the Pinhão river basin (North of Portugal) is attributed to three main influences (weathering, soil fertilization and urban pollution) which are described by factors obtained by Correspondence Analysis. The areal distribution of these influences is analyzed in six sampling epochs; differences between Autumn and Spring maps were generally attributed to changes in the water table.

1. Introduction

The composition of natural waters is determined by a number of processes, which include wet and dry deposition of atmospheric salts, evapotranspiration, water-soil and water-rock interactions. In inhabited areas, especially where there is intensive agriculture or industry, water composition is usually affected by fertilization and manuring, by leachates of solid waste, and by domestic and industrial effluents.

The contribution of each process affecting the water chemistry can be quantitatively assessed by mass balance models, as early recognized by Garrels & Mackenzie (1967) in a study of a pristine area (Sierra Nevada, USA) and lately by Pacheco & Van der Weijden (1996) in a study of an area with sizable anthropogenic input (Fundão, Portugal).

Factor Analysis and other eigenvector techniques are also used as methods for assessing the controls of water composition, especially in the study of huge hydrochemical data sets. Frequently the approach is strictly statistical, and although the analysis may identify the factors, the interpretation of these factors in terms of actual controlling processes is highly subjective.

Pacheco & Portugal Ferreira (1996) found significant correlations between factors obtained by Correspondence Analysis (C-vectors) and hydrochemical variables, for example the molar bicarbonate over silica ratio, which is characteristic

for particular water-mineral interactions. Based on the interpretation of these variables, they classified groundwater data sets from crystalline massifs as *systems of double influence* (silicate weathering and soil fertilization, under the background influence of atmospheric salt deposition). The discharge of domestic effluents directly into stream and river waters separates this type of contamination as an independent influence and, because of that, the samples collected in streams of the Pinhão river basin are here classified as a *system of triple influence*. Because samples were collected for three successive years (1993-1995), two times per year (April and October), seasonal variations could be analyzed.

2. Study area

The Pinhão river basin is located in the province of Trás-os-Montes (North of Portugal) and has an area of approximately 280Km² (Figure 1).

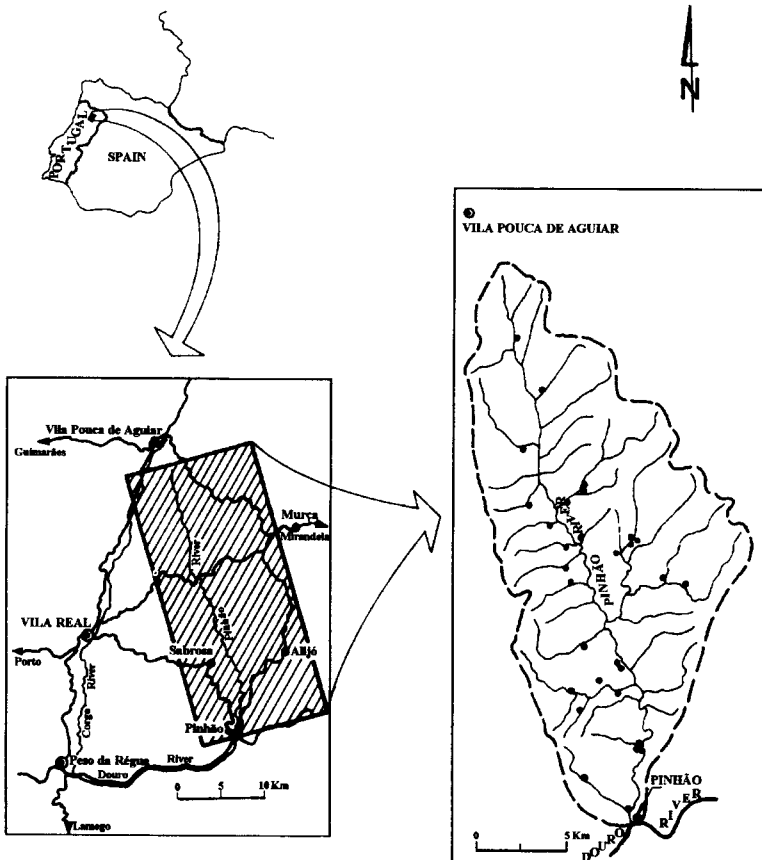


Figure 1. Geographical map of Portugal indicating the position of the Pinhão river basin. Blow-up of the area, with the major villages, connecting roads and drainage pattern in the basin. Small bullets represent sampling sites.

The northern area is dominated by hercynian granites and the southern area by paleozoic schists and graywackes (Figure 2). Granites are two mica, medium to coarse grained, sometimes with porphyroid texture; plagioclase varies in composition between albite and oligoclase/andesine. Soils developed from granites have variable amounts of kaolinite and gibsite (Alençoão *et al.*, 1996).

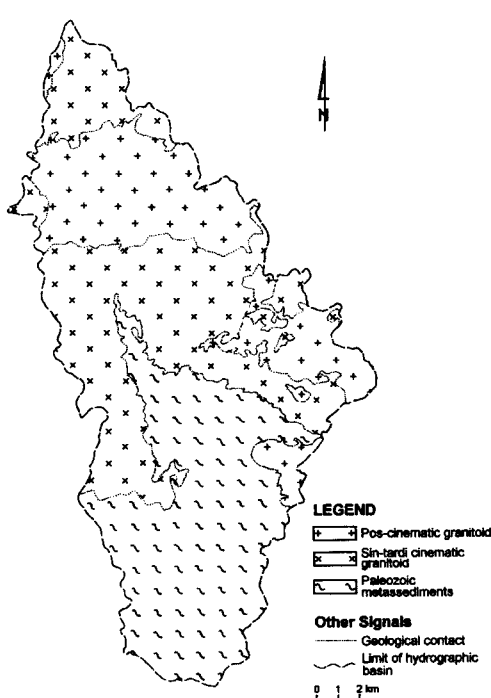


Figure 2. Geologic map of the Pinhão river basin; adapted from Sousa (1982) and Matos (1991).

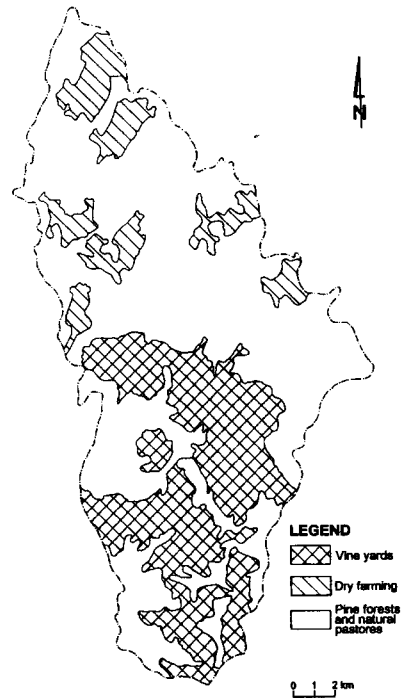


Figure 3. Land use map of the Pinhão river basin; adapted from Agroconsultores & Coba (1990).

Figure 3 is a simplified land use map of the Pinhão river basin. The northern area is occupied by pine forests where one can recognize small spots used for dry farming or natural pastures. The southern area is dominated by vine yards.

Human occupation is characterized by small settlements with no more than 200 people each, exceptionally reaching about 1000-1600 people in some small towns of the southern area (Sabrosa-1072, Favaiois -1207, Sanfins-1555).

3. Materials and Methods

3.1. SAMPLING AND ANALYSIS

Stream water samples were collected for three successive years (1993-1995), two times per year (April and October), in the Pinhão river basin. 29 sampling

sites were selected (cf. locations in Figure 1), 14 in granitic basins, 7 in schistose basins, and 8 in streams draining both granites and schists.

Chemical analyses were completed for major cations, major anions and dissolved silica and the results are given in Table 1. Sodium and potassium were determined by routine atomic emission spectrometry, magnesium and calcium by routine atomic absorption spectrometry, chloride, nitrate and silica by molecular absorption spectrometry; bicarbonate by titulimetry and sulphate by turbidimetry. House standards were used for calibration.

3.2. MATHEMATICAL AND CHEMICAL MODELING

Waters collected in the Pinhão river basin have drained granitic and schistose terrains and are contaminated to a certain extent by atmospheric input, domestic effluents and agricultural activity. Based on this background conditions, one might expect to find variance in major cation, major anion and dissolved silica concentrations assigned to: 1) changes in water composition caused by weathering; 2) changes in water composition due to human occupation; 3) changes in water composition related to land use. These changes are presumed to be represented by *C-vectors*, *factors* obtained by Correspondence Analysis, with the hierarchy suggest in Figure 4. On the top of this hierarchy one finds a *C-vector* that discriminates between contaminated and uncontaminated waters; one level below two *C-vectors* distinguish waters related to different weathering reactions and separate domestic waters from waters affected by soil fertilization or atmospheric salt deposition; on the third level the impact of specific cultures is anticipated.

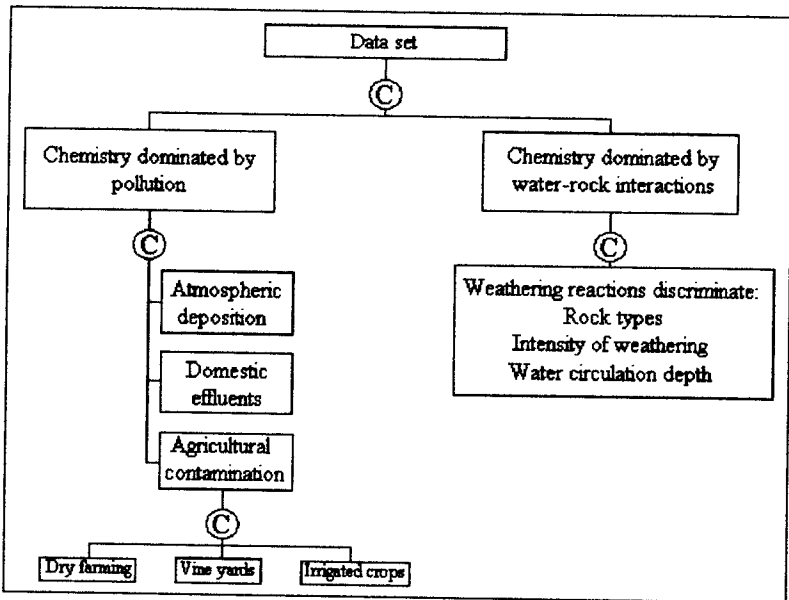


Figure 4: Dendritic structure of data sets, for stream water on crystalline massifs.

TABLE 1. Chemical composition of stream water samples collected in the Pinhão river basin. Concentration units in mg/l. (nd-not determined, vest-vestigial).

	APRIL 1993																				OCTOBER 1993																				APRIL 1994																			
	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17	P20	P22	P23	P24	P26	P28	P29	P30	P31	P32	P33	P35	P36	P37																															
Ca ²⁺	0.5	0.4	1.9	0.5	1.7	2.4	1.3	2.3	9.6	2.3	9.2	6.0	1.5	2.4	0.5	1.4	1.8	8.8	9.0	5.2	8.7	7.3	0.8	4.1	0.6	0.5	0.7	0.3	0.9																															
Fe ²⁺	0.1	0.3	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.4	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1																															
Mg ²⁺	0.4	0.3	0.6	0.4	0.9	1.0	0.8	1.3	5.2	1.2	4.8	3.2	0.6	1.4	0.5	0.8	1.0	6.4	5.8	3.5	4.5	4.5	0.5	1.6	0.5	0.4	0.4	0.4	0.6																															
K ⁺	50	vest	0.4	6.1	0.1	0.3	0.1	0.7	1.0	0.7	2.3	0.3	0.2	0.3	0.2	0.3	0.4	2.5	6.9	3.2	1.2	2.1	0.3	4.3	0.1	vest	vest	0.1	vest																															
Cl ⁻	3.6	3.6	3.6	7.0	4.0	10.6	3.6	7.0	7.0	3.6	7.0	7.5	7.0	3.6	3.6	3.6	23.1	24.6	14.0	14.1	8.5	3.6	8.9	3.6	3.6	3.6	3.6	3.6	7.0																															
HCO ₃ ⁻	19.5	9.2	10.4	15.3	20.3	7.9	18.3	11.6	51.2	18.3	67.7	53.1	7.9	14.0	10.4	7.3	13.5	27.1	65.9	23.2	30.5	40.6	12.2	23.7	10.4	7.3	7.9	6.7	10.4																															
NO ₃ ⁻	nd	nd	1.3	nd	nd	nd	nd	1.1	4.1	1.1	0.9	0.4	nd	5.8	0.3	0.6	0.3	10.0	8.9	10.2	12.8	12.7	0.2	0.6	nd	nd	nd	nd	nd																															
SO ₄ ²⁻	nd	0.7	5.3	nd	0.7	7.8	1.3	8.9	19.4	7.2	18.0	1.5	0.9	6.7	nd	6.0	6.9	29.3	23.4	10.3	13.1	15.0	nd	13.2	0.7	1.2	nd	1.2	1.6																															
SiO ₂	9.0	7.8	5.5	7.6	8.9	5.6	12.6	6.7	17.8	6.1	14.4	15.9	6.1	7.6	5.8	7.0	13.8	9.1	16.3	17.9	23.3	20.4	4.9	7.5	7.5	3.7	4.1	3.0	8.9																															
OCTOBER 1993																																																												
P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17	P20	P22	P23	P24	P26	P28	P29	P30	P31	P32	P33	P35	P36	P37																																
Ca ²⁺	1.6	0.8	9.6	0.8	2.8	3.1	1.4	2.2	12.9	1.8	12.4	7.9	7.6	4.5	5.0	3.0	3.1	9.8	13.1	8.1	12.4	10.2	1.0	4.0	0.8	1.2	0.7	0.8	1.2																															
Mg ²⁺	0.5	0.3	2.3	0.4	1.3	1.2	0.9	1.1	5.9	0.9	6.5	3.7	1.0	2.6	0.5	1.3	1.7	6.2	5.6	4.7	5.4	5.0	0.4	1.6	0.4	0.4	0.2	0.3	0.7																															
K ⁺	1.4	0.1	3.3	0.4	1.4	1.5	0.9	1.0	3.4	0.9	4.1	0.7	0.6	3.1	0.4	0.9	1.2	2.7	1.5	4.5	2.1	4.5	0.7	4.6	0.6	0.8	0.1	0.2	0.6																															
Na ⁺	4.7	3.2	9.2	5.2	7.7	7.4	6.0	5.0	14.3	4.7	17.8	10.6	5.0	12.9	3.8	6.7	7.0	19.0	39.8	12.0	12.5	15.3	3.3	9.0	4.0	5.0	3.0	3.3	6.2																															
Cl ⁻	6.4	4.2	13.6	5.2	11.3	12.1	4.3	5.9	7.9	6.1	14.4	9.1	5.7	18.4	4.9	7.1	9.2	20.4	35.0	15.5	13.6	15.9	4.1	13.5	5.0	7.0	3.0	4.4	7.8																															
HCO ₃ ⁻	7.9	3.1	4.9	8.5	11.0	4.9	15.9	6.7	62.2	3.7	75.6	38.4	29.9	6.1	17.1	2.4	6.1	43.9	106.8	30.5	32.3	35.4	6.1	12.9	6.1	6.1	4.9	3.1	7.3																															
NO ₃ ⁻	1.3	2.2	31.9	0.5	1.9	1.1	0.9	1.7	7.8	1.4	5.9	4.4	0.5	14.9	0.9	9.5	2.2	0.9	0.2	15.2	22.9	18.6	0.5	2.8	1.6	0.2	0.8	0.3	1.0																															
SO ₄ ²⁻	1.6	0.7	8.3	0.5	5.0	9.4	1.6	7.8	23.6	8.1	22.9	9.4	3.1	8.5	1.2	8.7	11.1	28.6	16.5	13.9	16.3	18.2	0.9	9.1	0.5	1.4	0.3	2.2	2.9																															
SiO ₂	6.8	6.7	8.8	9.4	10.8	9.8	12.2	6.3	18.9	6.1	16.2	16.8	7.6	12.1	8.1	7.2	7.9	15.6	19.7	16.8	19.8	17.0	6.2	8.5	7.7	6.3	5.8	5.4	9.8																															
APRIL 1994																																																												
P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17	P20	P22	P23	P24	P26	P28	P29	P30	P31	P32	P33	P35	P36	P37																																
Ca ²⁺	1.0	1.5	2.5	1.0	3.0	2.0	1.5	3.0	9.0	3.0	8.5	5.0	1.0	1.5	1.0	2.0	2.0	7.5	8.0	4.5	8.0	6.0	1.0	2.5	1.0	1.0	1.0	1.0	1.0																															
Mg ²⁺	1.0	1.5	1.0	1.0	2.5	1.0	1.0	2.5	5.5	2.0	4.5	3.0	0.5	1.0	1.0	2.0	1.5	5.5	5.5	3.5	4.5	4.5	1.0	1.5	1.0	1.0	1.0	1.0	1.0																															
K ⁺	0.6	0.6	1.2	0.4	0.8	0.8	1.4	0.8	2.2	0.4	0.4	0.6	0.4	0.6	0.6	2.4	5.4	1.4	1.2	2.0	0.8	3.6	0.6	0.4	0.4	0.4	0.4	0.2	0.2																															
Na ⁺	1.5	1.5	3.5	2.5	6.5	4.5	4.0	6.0	13.0	6.0	15.0	8.0	2.0	2.5	2.0	1.5	4.5	15.0	24.0	8.0	11.5	11.0	1.5	6.5	2.0	1.5	1.0	1.0	3.0																															
Cl ⁻	3.9	3.8	7.8	4.7	7.5	7.2	6.8	8.5	12.4	8.7	13.4	8.5	6.1	6.5	5.3	6.0	7.3	12.9	18.8	10.8	9.0	11.7	5.4	10.2	5.1	4.2	4.0	3.8	6.1																															
HCO ₃ ⁻	6.7	12.2	5.5	7.3	4.3	6.1	6.1	11.0	32.3	8.5	40.3	29.3	10.4	4.3	5.5	4.9	4.3	22.0	25.0	15.9	37.8	20.7	4.3	8.5	4.3	6.1	5.5	4.3	5.5																															
NO ₃ ⁻	0.0	0.0	0.6	0.0	1.3	0.0	0.0	3.5	11.1	4.0	3.5	0.7	0.0	0.3	0.3	0.7	2.7	14.2	34.2	11.8	12.5	16.3	0.6	1.2	2.3	0.0	0.0	0.0	0.0																															
SO ₄ ²⁻	Vest.	Vest.	4.0	0.3	2.6	5.3	3.2	8.4	21.6	7.5	19.5	5.3	1.5	1.8	0.0	3.9	5.6	28.1	23.3	7.5	10.8	13.4	Vest.	8.7	0.0	0.1	Vest.	0.0	1.1																															
SiO ₂	7.8	8.7	8.2	10.5	10.6	11.4	12.0	11.1	24.3	13.2	20.5	20.8	7.7	8.7	9.7	9.8	9.4	20.8	22.0	20.1	22.5	20.0	6.9	10.0	7.7	7.1	6.9	6.7	12.9																															

TABLE 1. Chemical composition of stream water samples collected in the Pinhão river basin. Concentration units in mg/l. (nd-not determined, vest-vestigial).

	OCTOBER 1994																																			
	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17	P20	P22	P23	P24	P26	P28	P29	P30	P31	P32	P33	P35	P36	P37							
Ca ²⁺	1.5	1.0	1.0	2.0	3.0	2.0	4.5	10.0	4.5				3.6	6.0	1.8		8.2	10.5	5.0	8.5	8.0	1.5	3.5	1.0	1.5	1.0	1.0	1.0	1.5							
Mg ²⁺	0.5	0.5	0.5	1.0	1.0	0.5	2.5	4.5	2.0				0.5	2.5	0.5		1.5	4.0	3.0	3.5	3.5	0.5	1.0	0.5	0.5	0.5	0.5	0.5	0.5							
K ⁺	0.7	0.1	0.3	0.5	0.8	0.7	1.5	1.4	1.5				0.2	0.6	0.5		1.7	8.0	1.5	3.2	3.1	1.4	3.7	0.7	1.3	0.2	1.3	0.4	0.4							
Na ⁺	4.0	3.5	4.5	6.5	7.0	6.0	9.0	13.0	9.0				6.2	11.7	5.1		13.1	51.0	9.5	11.5	15.5	8.0	7.5	3.5	4.5	3.0	3.0	5.0								
Cl ⁻	3.9	3.9	5.8	4.6	8.8	7.0	9.6	10.8	8.7				7.1	7.7	6.1		6.7	27.8	9.0	9.9	14.3	7.5	10.3	5.5	8.6	3.4	4.0	1.7								
HCO ₃ ⁻	9.5	6.1	8.5	6.1	14.0	9.8	17.1	46.4	10.4				14.6	7.3	5.8		15.2	92.7	20.7	28.1	24.4	15.9	12.2	7.4	6.1	6.1	6.8	6.1								
NO ₃ ⁻	0.5	2.8	nd	0.7	0.0	nd	4.4	vest	4.2				0.9	22.6	1.0		28.6	vest.	7.9	14.3	18.4	0.6	2.3	0.0	vest	0.0	nd	0.4								
SO ₄ ²⁻	nd	nd	0.01	3.40	2.90	11.30	19.90	15.80					3.10	10.00	3.70		11.30	1.00	10.40	14.90	10.90	1.20	7.10	0.60	1.60	nd	0.50	0.01								
SiO ₂	2.6	2.9	3.3	8.9	5.1	4.7	3.8	5.9	3.3				2.5	10.2	2.5		2.8	5.7	5.0	5.6	5.2	1.5	2.3	2.3	1.6	1.8	1.6	7.5								
APRIL 1995																																				
	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17	P20	P22	P23	P24	P26	P28	P29	P30	P31	P32	P33	P35	P36	P37							
Ca ²⁺	1.0	0.5	2.0	1.0	2.0	2.5	2.0	3.0	10.5	3.0	8.0	5.5	1.5	1.5	1.0	1.5	2.5	8.5	9.5	6.0	9.0	7.5	1.5	3.5	1.0	1.0	1.0	1.0	1.5							
Mg ²⁺	0.5	0.5	0.5	0.5	1.0	1.0	1.0	1.5	5.5	1.5	4.0	3.0	0.5	0.5	0.5	1.0	1.5	5.5	1.5	4.0	4.5	4.5	0.5	1.5	0.5	0.5	0.5	0.5	0.5							
K ⁺	0.2	0.2	0.6	0.2	0.4	0.4	0.4	0.8	1.4	0.8	1.6	0.4	0.4	0.6	0.4	0.6	0.6	2.4	5.6	1.6	1.4	1.8	0.6	3.8	0.4	0.2	0.2	0.2	0.5							
Na ⁺	2.5	2.5	4.0	3.5	6.0	6.0	5.0	6.0	13.0	6.0	13.0	8.5	3.5	3.0	3.0	3.5	5.0	15.5	31.0	9.0	12.5	12.5	2.5	7.5	3.5	2.5	2.5	2.5	4.5							
Cl ⁻	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.7	0.0	5.7	0.0	0.0	0.0	0.0	0.0	0.0	11.7	21.0	1.0	5.1	6.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0							
HCO ₃ ⁻	9.8	9.2	12.2	12.2	23.2	20.1	20.7	22.7	65.9	23.2	59.2	48.2	12.8	12.2	12.2	14.0	22.3	52.5	47.0	43.3	55.5	45.0	12.2	38.4	13.4	9.8	9.8	10.4	15.9							
NO ₃ ⁻	0.2	0.4	3.4	0.3	0.7	0.4	0.3	3.8	9.8	3.7	1.9	2.2	0.0	0.6	0.2	1.5	2.4	13.3	26.7	11.8	14.2	15.7	0.5	1.0	0.0	0.1	0.0	0.1	0.6							
SO ₄ ²⁻	1.9	1.8	3.3	1.7	2.9	4.1	2.9	4.6	8.1	4.7	8.1	3.7	2.9	3.3	2.0	3.7	4.2	9.3	11.6	5.2	6.5	6.7	2.0	3.7	1.8	2.0	1.8	1.8	2.3							
SiO ₂	6.4	10.0	8.3	10.4	10.5	10.8	9.8	8.6	15.1	8.8	18.8	13.2	8.0	8.8	7.8	10.2	7.7	18.4	19.3	15.6	10.1	17.0	5.6	9.8	7.6	6.6	5.5	5.2	11.7							
OCTOBER 1995																																				
	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17	P20	P22	P23	P24	P26	P28	P29	P30	P31	P32	P33	P35	P36	P37							
Ca ²⁺	1.5	1.0	4.5	1.0	2.0	3.0	2.5	5.0	10.5	5.0			1.5	2.0	1.5		4.0	11.5	5.5	8.5	8.5	2.0	3.5	1.0	1.0	1.0	1.0	1.5								
Mg ²⁺	0.5	0.5	1.5	0.5	1.0	1.5	1.0	5.0	5.5	3.0			0.5	1.0	0.5		2.5	6.0	4.0	4.5	4.5	0.5	1.5	0.5	0.5	0.5	0.5	0.5								
K ⁺	0.8	0.4	5.4	0.6	0.6	1.0	1.0	1.8	1.8	1.8			1.0	1.6	0.8		1.6	12.0	2.2	2.0	3.8	1.8	4.0	1.0	1.0	0.6	0.4	0.6								
Na ⁺	4.0	3.5	18.0	4.0	7.0	10.0	15.5	11.5	15.5	11.0			4.5	3.5	4.0		8.5	50.0	10.5	13.0	9.5	4.5	7.5	4.0	3.0	3.5	5.5	6.6								
Cl ⁻	5.1	3.9	16.9	5.6	9.4	9.6	8.9	10.9	11.8	13.6			6.0	7.1	6.5		10.0	28.0	11.8	13.3	18.9	7.6	10.3	5.2	4.5	4.1	6.5	6.5								
HCO ₃ ⁻	7.3	7.3	7.3	6.1	7.9	14.6	37.8	25.6	64.7	19.5			5.5	8.5	4.3		14.6	126.3	30.5	37.2	7.3	9.8	15.3	6.1	6.7	6.7	7.3	7.3								
NO ₃ ⁻	0.5	0.4	28.0	0.5	0.2	0.7	0.9	3.6	0.0	3.9			1.2	1.3	1.7		3.8	0.3	8.1	11.9	16.8	0.6	3.9	0.7	0.2	0.2	0.6	0.6								
SO ₄ ²⁻	1.7	1.1	9.1	1.3	5.3	10.5	1.8	12.0	16.5	12.4			4.3	1.0	1.7		11.1	19.6	8.8	11.5	11.6	1.9	6.8	1.2	1.1	1.1	3.9	3.9								
SiO ₂	4.4	5.0	6.9	7.0	7.9	10.8	9.5	6.7	14.0	6.2			5.4	10.4	5.5		6.7	15.5	11.4	12.4	12.6	3.9	5.1	4.5	4.2	4.2	3.4	7.0								

Variance distribution is assumed to be hierarchic because the top-level C-vector is predicted to be the vector with the highest percentage of variance, the bottom-level C-vector is predicted to be the vector with the lowest percentage of variance, and so forth. If changes in water composition produced by one of the above selected causes are not significant, the corresponding C-vector is foreseen to be absent; for example, the top-level C-vector is not expected to incorporate the model if huge levels of contamination affect the whole sampled area.

The conceptual vector model of Figure 4 is checked in three consecutive steps:

- 1) C-vectors obtained as output of Correspondence Analysis are used as independent input variables of a linear multiple regression model, which has as dependent variable one relevant hydrochemical variable.
- 2) If regression parameters (the b 's) are low for all C-vectors but one, this vector is represented by the hydrochemical variable if the corresponding b is significant and the coefficient of multiple determination (or *goodness of fit*), R^2 is close to 100%
- 3) Because there are four C-vectors, Multiple Regression Analysis is applied four times with four different hydrochemical variables. Full validation of the vector model is obtained when each C-vector is represented by a different variable.

Hydrochemical variables are attached to C-vectors as explained bellow.

In every cases concentrations are expressed in the *eq/l* scale.

- 1) The top-level C-vector in Figure 4 is attached to the percentage of pollution referred in Sousa Oliveira & Portugal Ferreira (1996) as

$$\% - \text{Pollution} = \frac{[Cl] + [SO_4] + [NO_3]}{[Cl] + [SO_4] + [NO_3] + [HCO_3]} \times 100 \quad (1)$$

Because chloride, sulphate and nitrate concentrations in water, are usually derived from pollution sources and the bicarbonate concentration is essentially related to the hydrolysis of silicates, samples with %-pollution scores higher than 50% are marked as contaminated, while those with scores bellow 50% are labeled as uncontaminated.

- 2) The two C-vectors at the second level are attached to the percentage of chloride in pollution

$$\%Cl = \frac{[Cl]}{[Cl] + [SO_4] + [NO_3]} \times 100 \quad (2)$$

and to the molar bicarbonate over silica ratio ($[HCO_3]/[SiO_2]$).

The higher is the %Cl more important is the contribution of domestic effluents (and/or atmospheric salt deposition) to pollution; the lowest %Cl scores characterize the impact of soil fertilization, because sulphate and nitrate are important anion constituents of commercial fertilizers.

Garrels (1967) showed that dissolved HCO_3 , dissolved SiO_2 and its ratios is a good diagnostic parameters for particular water-mineral interactions.

- 3) The bottom-level C-vector in Figure 4 is attached to the $[\text{SO}_4]/[\text{NO}_3]$ ratio because fertilizers used in dry farming have $[\text{SO}_4]/[\text{NO}_3] \approx 0$ while those used in irrigated crops and vine yards have ratios around 3 and 6, respectively.

4. Results and Discussion

Correspondence Analysis (CA) is performed and hydrochemical variables are calculated from data in the Table 1. Multiple Regression Analysis (MRA) is applied as explained above and the results are presented in Table 2.

The variance absorbed by C-vectors is always higher than 89%. In all the cases but one ($[\text{SO}_4]/[\text{NO}_3]$ in April 1993), it is clearly recognized which is the C-vector correlative to a given hydrochemical variable because the regression parameter in that C-vector is high, when compared with those in the other C-vectors. In 14 of 19

TABLE 2. Results of Multiple Regression Analysis (MRA). C-vectors (C_x) are used as independent variables and hydrochemical variables as dependent variables. N_i is the total number of samples in the data set and N_m the number of samples used in the MRA calculations; $N_i - N_m$ represent the number of anomalies in each hydrochemical variable. R^2 is the coefficient of multiple determination. Relevant regression parameters are represented in bold face. The program used to perform C.A. was adapted from Bencrezi (1973), the MRA - model was calculated by STATISTICA software.

April 1993: $C_1+C_2+C_3+C_4=39.9+19.6+17.2+15.7=92.4\%$ of system variance							
	N_i	N_m	C_1	C_2	C_3	C_4	$R^2(\%)$
%-pollution	29	29	0.91	0.36	0.41	0.22	98.9
%Cl ^{a)}	15	15	0.15	0.64	0.40	0.30	84.8
$[\text{HCO}_3]/[\text{SiO}_2]$	29	29	0.14	0.26	0.90	0.28	71.9
$[\text{SO}_4]/[\text{NO}_3]^b)$	17	12	0.32	0.37	0.41	0.49	79.2
a) group of samples with %-Cl<80%							
b) 12 samples with $\text{NO}_3=0$							
October 1993: $C_1+C_2+C_3=52.8+23.0+13.3=89.1\%$ of system variance							
	N_i	N_m	C_1	C_2	C_3		$R^2(\%)$
%-pollution	29	29	0.78	0.47	0.38		98.8
%Cl	29	26	0.18	0.71	0.43		93.5
$[\text{SO}_4]/[\text{NO}_3]$	29	23	0.47	0.17	0.90		85.1
April 1994: $C_1+C_2+C_3=56.8+20.3+14.5=91.6\%$ of system variance							
	N_i	N_m	C_1	C_2	C_3		$R^2(\%)$
%Cl	29	29	0.90	0.14	0.17		95.4
$[\text{HCO}_3]/[\text{SiO}_2]$	29	29	0.24	0.90	0.02		89.7
$[\text{SO}_4]/[\text{NO}_3]^b)$	20	20	0.29	0.18	0.75		58.9
a) 9 samples with $\text{NO}_3=0$							
October 1994: $C_1+C_2+C_3=52.5+23.4+14.2=90.1\%$ of system variance							
	N_i	N_m	C_1	C_2	C_3		$R^2(\%)$
%Cl	24	24	0.83	0.38	0.14		95.8
$[\text{HCO}_3]/[\text{SiO}_2]$	24	24	0.36	0.23	0.68		63.2
$[\text{SO}_4]/[\text{NO}_3]^b)$	18	16	0.19	0.87	0.26		68.7
a) 6 samples with $\text{NO}_3=0$							
April 1995: $C_1+C_2+C_3=66.9+16.7+8.2=91.8\%$ of system variance							
	N_i	N_m	C_1	C_2	C_3		$R^2(\%)$
%-pollution	29	29	1.01	0.34	0.16		94.3
%Cl ^{a)}	7	7	0.40	0.02	0.87		93.4
$[\text{HCO}_3]/[\text{SiO}_2]$	29	29	0.29	0.76	0.14		86.5
a) 22 samples with Cl=0							
October 1995: $C_1+C_2+C_3=60.6+19.7+10.5=91.1\%$ of system variance							
	N_i	N_m	C_1	C_2	C_3		$R^2(\%)$
%-pollution	24	24	0.93	0.49	0.23		95.5
%Cl	24	23	0.19	0.32	0.72		92.0
$[\text{HCO}_3]/[\text{SiO}_2]$	24	21	0.47	0.80	0.07		93.0

cases the goodness-of-fit of the MRA-model (R^2) is higher than 84%. %Cl is always a significant hydrochemical variable; $[\text{HCO}_3]/[\text{SiO}_2]$ is absent in one sampling period and the other variables in two periods.

Figure 5 shows the spatial distribution of %-pollution scores in six sampling epochs. Contamination is higher in the southern area probably because viniculture produce more impact on stream water chemistry than dry farming (see also Figure 3); besides, population is more concentrated in the South. Except in the year of 1994, %-pollution increases when samples are collected after a dry season (sampling in October) and decreases when sampling was made after a humid season (April). In our opinion, that is a direct consequence of the hydrologic and land use cycles: a) In the area, the fertilizers are applied in Spring or early Autumn and stay in the soil until they became leached by Autumn rains; this produces the increase in the October scores. b) Continuous leaching during Winter cleans-up the soils and, consequently, stream waters in April are less contaminated; that is particularly visible in the period October 1994 - April 1995. The unexpected high scores of April 1994 are interpreted as the result of an early soil - washing caused by sudden occurrence of precipitation



Figure 5. Spatial distribution and seasonal variation of %-pollution. We used SURFER software to perform the surface maps, adopting kriging as interpolation method.

after seed-sowing, although distribution of these scores is not statistically significant as %-pollution is not assigned to any C-vector (cf. Table 2).

Distribution of %Cl values are shown in Figure 6; because 22 of 29 samples collected in April 1995 have anomalous zero chloride concentrations, the corresponding %Cl iso-contour map is not presented. Scores are high in the northern area and low in the southern area. Changes in climatic conditions from April to October seem to have little effect on the pattern of distribution maps, mainly in the southern area.

High %Cl scores in the northern area are attributed to atmospheric contamination, while low scores in the southern area are ascribed to agricultural activity (viniculture). The small spots of high %Cl surrounded by areas where %Cl is much lower are identified as the areas where domestic contribution is predominant; for example, contamination produced by Sabrosa domestic effluents is clearly foreseen in the small elliptical zones with %Cl between 60 and 70% located in the southern part of the October 1994 and October 1995 maps.

Seasonal changes in the pattern of %Cl dispersion maps are probably related to the type of soil uses practiced in the northern and southern areas: a) the non

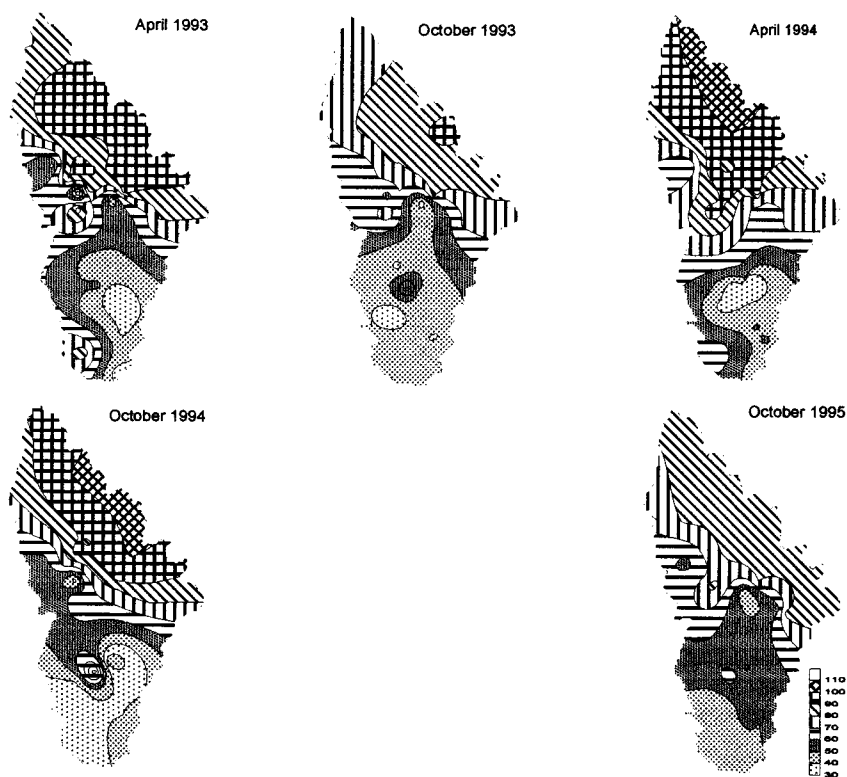


Figure 6. Spatial distribution and seasonal variation of %Cl; additional information on figure 5.

existing changes in the southern area are assigned to the fact that vine yards farming imposes a long standing signature on the soils, with its conservative influence over stream water composition; b) changes in the northern area are generally characterized by a decrease in the %Cl of samples collected in October (except October 1994). This reduction is probably caused by an increase in sulphate and nitrate concentrations related to fertilization of "non-perennial" cultures like wheat and rye; these cultures are normally sowed in late September and, as a consequence of top-dressing fertilization, one might indeed envisage changes in the chemistry of stream waters when sampling is made in October.

The $[\text{HCO}_3]/[\text{SiO}_2]$ ratio changes with time as it is illustrated in Figure 7; all maps are statistically significant, except that one of October 1993 (cf. second block of Table 2).

With the exception of April 1994, the $[\text{HCO}_3]/[\text{SiO}_2]$ scores are higher in the schists. A possible cause for this difference lies on the fact that weathering in the granites is controlled by plagioclase, whereas in the schists the biotite hydrolysis might determine the chemistry of groundwater.

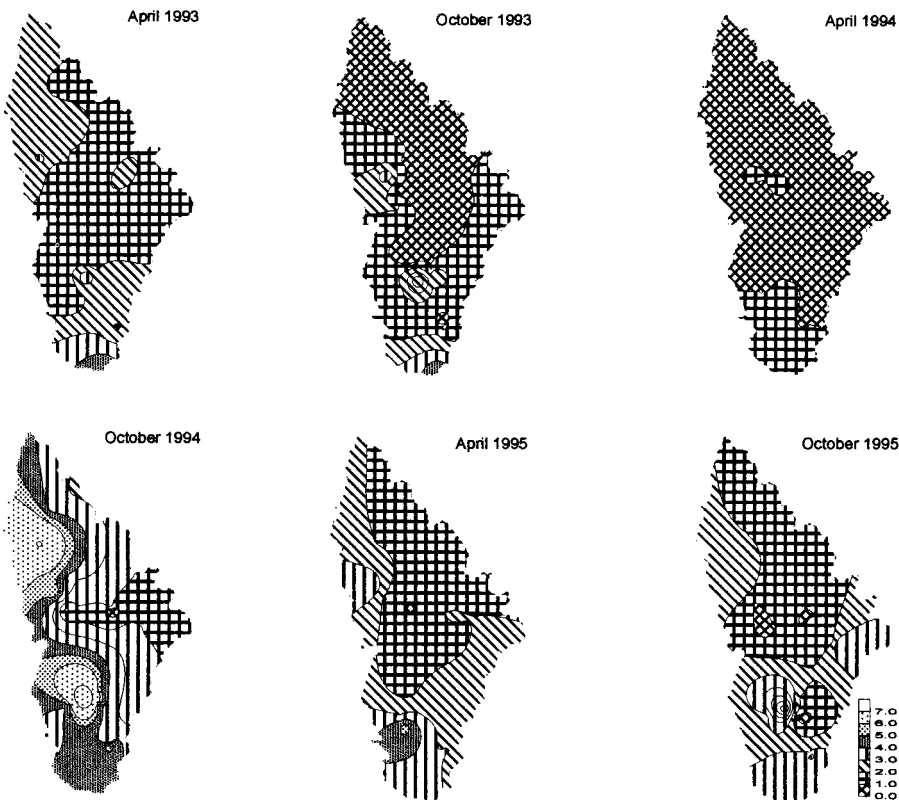


Figure 7. Spatial distribution and seasonal variation of $[\text{HCO}_3]/[\text{SiO}_2]$; additional information on figure 5.

Alencão *et al.* Established, for the Pinhão river basin, a significant correlation between the $[\text{HCO}_3^-]/[\text{SiO}_2]$ ratio and the mean precipitation occurred four months before sampling. Based on these mean values of precipitation, sampling epochs were defined as *after dry* (April 1993, October 1994 and October 1995) or as *after humid* (October 1993, April 1994 and April 1995) seasons.

The lowest scores, to be found in the granites after wet periods, range between the theoretical values found for the hydrolysis of albite-oligoclase into kaolinite and gibbsite, meaning that weathering is represented by reactions occurred in the soil. The highest scores, which are characteristic for the dry periods, probably result from water-rock interactions, naturally processed at more significative depths.

The information regarding the $[\text{SO}_4]/[\text{NO}_3]$ ratios is so scarce and highly heterogeneous that any sound explanation for their distribution is out of question.

5. Final Remark

It is to be remarked that combined application of Correspondence Analysis, Linear Multiple Regression Analysis and Hydrochemical Modeling might be used with stream water chemical compositions in order to explain its affiliation on weathering reactions, soil fertilization, domestic effluents and atmospheric inputs. This essay produced promising and convincing results, especially to evaluate the importance of each of the controlling processes.

6. Acknowledgments

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7. References

- Agroconsultores & Coba (1990) *Carta de Solos, Carta do Uso Actual da Terra, e Carta de Aptidão da Terra do Nordeste de Portugal*, Universidade de Trás-os-Montes (PDRITM), Vila Real.
- Alencão, A. M. P., Pacheco, F. A. L. & Portugal Ferreira, M. R. (1996) Variação da razão bicarbonato/silica, na água, e sua relação com a reacção de alteração em solo e subsolo granítico, *3º Congresso da Água e VII Silubesa*, **III**, 29-35.
- Garrels, R. M. & Mackenzie F. T. (1967) Origin of the chemical compositions of some springs and lakes, In W. Stumm, *Equilibrium Concepts in Natural Water Systems*, Am. Chem. Soc.
- Matos, A. V. (1991) *A Geologia da Região de Vila Real*. Tese de doutoramento, UTAD, Vila Real.
- Pacheco, F. A. L. & Portugal Ferreira, M. R. (1996) Sistemas hidroquímicos com dupla influência: sua definição e interpretação no contexto da análise de correspondências, *3º Congresso da Água e VII Silubesa*, **III**, 177-185.
- Pacheco, F. A. L. & Van der Weijden, C. H. (1996) Contributions of water-rock interactions to the composition of groundwater in areas with a sizable anthropogenic input. A case study of the waters of the Fundão area, central Portugal, *Water Resouces Research* (in press).
- Sousa, M. B. (1982) *Litostratigrafia e Estrutura do Complexo Xisto-Graváquico ante-Ordovícico - Grupo do Douro (Nordeste de Portugal)*, Tese de doutoramento, Universidade de Coimbra.
- Sousa Oliveira, A. & Portugal Ferreira M. R. (1996) A hidroquímica das águas meteóricas da região de Pedras Salgadas - Aplicação da análise de correspondências com vista à sua caracterização, *3º Congresso da Água e VII Silubesa*, **III**, 131-138.