# Spatial and temporal heterogeneity in the Alqueva reservoir, Guadiana river, Portugal

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#### ABSTRACT

#### Spatial and temporal heterogeneity in the Alqueva reservoir, Guadiana river, Portugal

This study aims to assess the physico-chemical variability of the Alqueva reservoir during its initial filling period. The dataset consists of analytical results from an 11 month survey (Mar 2003-Jan 2004) conducted in the water body, at three levels of depth in the several tributaries and in the discharge section. 21 parameters were monitored on a monthly base, in order to understand the temporal and spatial variability. Another goal of this work was to use a multivariate statistical approach to help understand the relationships between water quality parameters, to group zones according to their similarities and to distinguish between wet and dry season conditions. FA/PCA needs 6 VF/PC to point out 74 % in the wet season, and 7 VF/PC to explain 78.6 % of variance in the dry season. FA/PCA allows grouping the selected parameters according to common features. As a result, mineral content is indicated as the principal source of variability in the wet season, while oxygenation plays the main role in the dry season. DA renders an important data reduction using 10 parameters to provide 93.2 % right assignations during temporal analysis. DA assigns temporal variability to the consequences of water balance on ambient salinities, to stratification influences and to surface runoff. Also, it uses only 4 parameters to yield 71.3 % right assignations during the spatial analysis in the dry season. Conductivity declines in the lacustrine zone, while CBO5, pH and Temperature vary principally in the vertical sense. However, such a spatial pattern is not static. It can become either more defined during the dry season, or less evident during the expansion of the lotic conditions in the rainy period (late spring and summer). Seasonal processes of stratification/mixture determine the temporal changes in the lacustrine zone. The system seems to be affected by periodic pulses of modifications produced by intensive rains and drought. Thus, limnological understanding of these questions is a prerequisite for making wise judgments about reservoir management.

Key words: Alqueva reservoir, water quality, dry season, wet season, principal component analysis, factor analysis, discriminant analysis.

#### RESUMEN

#### Heterogeneidad espacial y temporal en el embalse de Alqueva, río Guadiana, Portugal

Este estudio apunta a determinar la variabilidad fisco-química del embalse de Alqueva en su período de llenado inicial. El conjunto de datos consiste en resultados analíticos a partir de los primeros once meses de muestreo (marzo de 2003-enero de 2004) conducida en el cuerpo del agua, en tres niveles de profundidad; en los varios tributarios y en la sección de la descarga. 21 parámetros se han supervisado en una base mensual, para entender la variabilidad temporal y espacial. Otra meta de este trabajo fue el utilizar un acercamiento estadístico multivariado para ayudar a entender las relaciones entre los parámetros de la calidad del agua; para agrupar zonas según sus semejanzas y distinguir entre las condiciones de las estaciones húmeda y seca. FA/PCA necesita 6 VF/PC para precisar 74 % de la estación húmeda, y 7 VF/PC para explicar 78.6 % de la variación en la estación seca. FA/PCA permite agrupar los parámetros seleccionados según características comunes. Como resultado el contenido mineral se señala como la fuente principal de la variabilidad en la estación húmeda, mientras que la oxigenación desempeña el papel principal en la estación seca. DA rinde una reducción de datos importante usando 10 parámetros para producir 93.2 % de clasificaciones correctas durante análisis temporal. DA asigna variabilidad temporal a las consecuencias

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del balance del agua en salinidades, a las influencias de la estratificación y a la salida superficial. Además, utiliza solamente 4 parámetros para rendir 71.3 % clasificaciones correctas durante el análisis espacial en la estación seca. La conductividad decae en la zona lacustre, mientras que CBO5, el pH y la temperatura varían principalmente en el sentido vertical. Sin embargo, un patrón tan espacial no es estático. Puede hacerse mas definido durante la estación seca, o menos evidente durante la expansion de las condiciones loticas en el período lluvioso (fin de primavera y verano). Los procesos estacionales de la mezcla de la estratificación determinan los cambios temporales en la zona lacustre. El sistema parece afectado por pulsos periódicos de las modificaciones producidas por las lluvias intensivas y sequía. Así la comprensión limnologica de estas preguntas es un requisito previo para hacer juicios sabios sobre la gerencia del embalse.

**Palabras clave:** Embalse de Alqueva, calidad del agua, estación seca, estación húmeda, análisis de componentes principales, análisis factorial, análisis discriminante.

# **INTRODUCTION**

As well as creating a new water resource, the construction of a dam may also involve substantial modifications to the environment, during both construction and subsequent operation (Crouzet & Leonard, 1999; Bergkamp et al., 2000). These changes include increases in residence time, temperature, stratification, and reduction in turbulence, most often a decrease in particles and turbidity, and sometimes an increase oinautochthonous primary production (Friedl & Wüest, 2002). The variability and complexity of these changes is reflected in the water quality. If water quality deteriorates in a reservoir, it may become unsuitable for its original purposes and costly measures may be required to combat the problem. It also constitutes a threat to the downstream ecosystem (Ferreira, 1999). The water quality of reservoirs is controlled by several factors, among which the interaction of the lacustrine end with the catchment area plays an important role (Carpenter & Cottingham, 1997; Wetzel, 1993). This feature assumes particular importance in newly flooded areas. Thus, the success of reservoir management and restoration projects depends on the detection of spatial and temporal changes in reservoir status that reflect changes in the surrounding environment. Seasonal climate changes are the most relevant, particularly rainfall and solar heating, resulting in seasonal variations in water quality (Chapman, 1996). The assessment of long term trends (seasonal, annual) is related directly to the reservoir management strategies required to understand the processes occurring within the

reservoir and to provide more detailed information on a variety of indicators of reservoir condition (Hoyos & Comín, 1999). This seasonal monitoring assumes particular importance in the Portuguese southern semi-arid areas, where the river discharge may range from zero in the dry season to high discharge rates during the rainy season (Morais, 1995; Bernardo & Alves, 1999). Subjected to a great variability of the hydrologic regime, tributaries experiment wide ranges in physical-chemical and biological parameters (Morais, 1995), affecting the reservoirs downstream. Therefore, the understanding of various phenomena relating to the characteristics of the reservoir and its catchment area is the most basic step in evaluating water quality and judging specific problems (Hwang et al., 2003).

The chemistry of standing waters is intimately linked to the physical processes occurring within the water body as well as in the atmosphere and the catchment. Physical features with high seasonal variation such as light and temperature play key roles in most chemical transformations, either by accelerating chemical or enzymic reactions or by promoting photosynthesis (Boulton & Brock, 1999). When changing a stretch of a river to a reservoir, the slowdown of the flow subsequently evokes particle settling, turbidity decreases and light transmissivity increases, enhancing in situ primary production. Thus, from the headwater of the reservoir to the dam the river changes from an allochthonous-dominated system to a more lacustrine system, where autochthonous production of organic matter dominates (Friedl & Wüest, 2002). Therefore, the existence of progressive physical, chemical and biological changes along the main axis of the reservoir frequently reflect strong spatial gradients. Seasonal events can make the spatial structure even more complex, both vertically and horizontally (Catalan & Fee, 1994; Wetzel, 1993). Due to those spatial and temporal variations, a monitoring programme that will provide a representative and reliable estimation of the quality of reservoir water is necessary (Simeonov et al., 2003). The usual situation is the measurement of multiple parameters, taken at different monitoring times and from many monitoring stations. Therefore, a complex data matrix is frequently needed to evaluate water quality (Chapman, 1996). Furthermore, it is a common experience to face the problem of determining whether a variation in the concentration of measured parameters should be attributed to pollution (man-made, spatial) or to natural (temporal, climatic) changes. Also, it is necessary to determine which parameters are the most significant for describing such spatial and temporal variations, the sources of pollution, etc. Therefore, the use of multivariate techniques has increased in recent years, mainly due to the need to obtain appreciable data reduction for analysis and decisionmaking (Chapman, 1996, Vega et al., 1998, Pesce & Wunderlin, 2000, Helena et al., 2000).

In this context, this study aims to assess physical-chemical seasonal variability of the Alqueva reservoir (Guadiana river basin). Knowing that reservoirs formed by river impoundment undergo great changes in water quality during the early stages of their formation whilst a new ecological balance is becoming established, EDIA (Empresa de Desenvolvimento e Infra-Estruturas de Alqueva), with the beginning of the filling phase (February 2002), implemented a monitoring programme that provides an evaluation of spatial and temporal variations in water chemistry and biology. This paper documents water quality in the features of input flux, state and discharge, during 11 months in the filling phase. Another goal of this work is to use a multivariate statistical approach to aid the understanding of the relationships between water quality parameters, to group zones according to

**Table 1.** Land use in the Portuguese side of the catchmentarea using CORINE land cover classes. Usos de la tierra en ellado portugués de la cuenca utilizando las clases de coberturaCORINE.

Classes	% ocupation
Artificial Areas	0.75
Agriculture	69.83
Semi-natural	28.50
Aquatic Areas	0.89
No information	0.03
Total	100

their similarities and to distinguish between wet and dry season conditions.

# STUDY AREA

The Alqueva reservoir, located in southern Portugal along 83 km of the main course of the Guadiana river, constitutes the biggest artificial lake on the Iberian Peninsula. It can store  $4500 \text{ hm}^3$  of water, with a dentiform surface of 25000 ha. The catchment area is 55 000 km<sup>2</sup>. The Portuguese side covers only  $4310 \text{ km}^2$ .

During the study period, the climate on the Portuguese side of the catchment area was characterized by a mean temperature of 17.5 °C ranging from 4.5 °C in January to 33.3 °C in August. The total precipitation was 358mm, and the potential evapotranspiration 271mm. The annual insulation is 2859 h. The dry season extends from May to September. The bed rocks are dominated by granite and gneiss mainly covered by Aluvissolos and Litossolos. The Land use in the Portuguese side of the catchment is presented in Table 1, and it was calculated using CORINE land cover classes. Notice that 69.8 of the catchment is used for agriculture, while the semi-natural areas only represent 28.5 %.

# METHODOLOGY

# Sampling and analytical procedures

In total, 8 collection sites were established, 4 with lentic characteristics sampled at 3 levels of depth (surface, middle and bottom) and 4 with lotic



Figure 1. Map of the reservoir and sampling site locations. Mapa del embalse y situación de las estaciones de muestreo.

characteristics sampled from the margin (Fig. 1). The sites Sr.<sup>a</sup> da Ajuda (SA), Alcarrache (Alc) and Álamos (Ala), provide a monitorization of the input flux. Albufeira Mourão (Mou) and Alqueva Montante (AM), located in the water body, provide the state monitoring, while Alqueva Jusante (AJ) provides the outlet monitoring. The sites Ardila (Ard) and Moinho das Barcas (MB) are useful in evaluating the water quality in the downstream ecosystem. They also aid in establishing a reference of water quality prior to the construction of the Pedrogão Reservoir, which will be located immediately downstream from the Alqueva Dam. Monthly monitoring was done from March 2003 to January 2004. Vertical profiles were made of Temperature, Dissolved Oxygen, pH and Conductivity, in sites located in the water body, using a 3L Van Dorn bottle to collect water samples, and a WTW 350i probe, with a pH electrode WTW pH Sentix 41-3 and a combined Conductivity –Oxygen probe WTW ConOx- 3 to conduct the measurements. Samples for analysis were collected at the surface, the middle and the bottom. At sites located in water streams, measurements and sampling where done from the bank. In the laboratory, 16 parameters were determined by using official recommended methods of analysis (A.P.H.A., 1998). Measured parameters include: Nitrate (4500-NO<sub>3</sub><sup>-</sup> E.); Ammonium (4500-NH<sub>3</sub> F.); Total Nitrogen (TN) [Kjeldahl nitrogen (4500-Norg) + nitrates); Soluble Reactive Phosphorus (SRP) (4500-P E.); Total Phosphorus (TP) (4500-P E., after acid digestion); 5-day Biological Oxygen Demand (BOD-5) (5210 B.); Chemical Oxygen Demand (COD) (5220 C); Permanganate Oxidizable Compounds (POC) (Rodier, 1981); Magnesium (Hardness-Calcium); Calcium (3500-Ca D); Chloride (4500-Cl<sup>-</sup> B.); Hardness (2340 C.); Alkalinity (2320-B); Total Dissolved Solids (TDS) (2540-C) and Total Suspended Solids (2500 D.-TSS).

## Statistical treatment of data

Statistical analysis was applied on experimental data normalized to zero mean and unit variance (standardized data) in order to avoid misclassifications arising from the different orders of magnitude. We studied the correlation structure between variables using the Pearson coefficient. The multivariate approach was performed using two techniques: factor analysis (FA), including principal component analysis (PCA) and discriminant analysis (DA). Principal component analysis (PCA) allowed ending out associations between variables, thus reducing the dimensionality of the data table. This is accomplished by diagonalization of the correlation matrix of the data, which transforms the 19 original variables into 19 uncorrelated (orthogonal) ones (weighed linear combinations of the original variables) called principal components (PCs). The eigenvalues of the PCs are a measure of their associated variance, the participation of the original variables in the PCs is given by the loadings, and the individual transformed observations are called scores (Johnson and Wichern, 1992; Reis, 1998; Vega et al., 1998; Helena et al., 2000; Pesce & Wunderlin, 2000). In practice, FA follows PCA. The main purpose of FA is to reduce the contribution of less significant variables in order to simplify even more of the data structure coming from PCA, at the cost of a loss of orthogonality. This last purpose was achieved by performing a Varimax rotation in the axis defined by PCA. Discriminant analysis (DA) provides statistical classification of samples. We can use DA if we know in advance the membership of objects to particular groups or clusters (i.e., the temporal or spatial ownership of a water sample as determined from its monitoring time or station). We can construct a discriminant function for each group; this function has the form presented in Johnson and Wichern (1992). It represents a surface dividing our data space into regions; then samples sharing common properties will be grouped into the same region with a decision boundary separating two or more groups. The efficiency of these discriminant functions can then be checked with the same data set using the cross validation method (Miller & Miller, 2000). DA was performed on each data matrix by using the standard and the stepwise modes. The best discriminant function for each situation was selected considering the goodness of the classification matrix and the number of parameters needed to reach such a matrix. The statistical package SPSS 11.5 was used for calculation.

## **RESULTS AND DISCUSSION**

Our first approach to establish the parameters associated with temporal variation was using



Figure 2. Temperature profiles at Alqueva Montante from March 2003 (1) to January 2004 (11). Perfiles de temperatura de Alqueva Montante desde Marzo de 2003 (1) a Enero de 2004 (11).

the Pearson correlation coefficient. To perform a Pearson evaluation, each season was transformed into a numerical value in the data matrix (Wet = 1 and Dry = 2); this numerical variable was then correlated (pair by pair) with all the measured parameters. The results show that the water temperature exhibits the highest correlation coefficient (r = 0.551; p < 0.01; n = 176) with the season. In addition to the temperature, we observed seven additional parameters having significant correlation with the season (p < 0.01): TDS (r = 0.536), Alkalinity (r = 0.398), TP (r = -0.307), Conductivity (r = 0.287), Calcium (r = 0.279), Magnesium (r = 0.213), and SRP (r = -0.195). So far, this group could be taken as representing the major source of temporal changes in water quality. Many of these correlations can be explained in view of the climatic features associated with the wet season (October to April) and dry season (May to September). So it is evident that the water temperature reflects the atmospheric temperature, and that this parameter presents the most significant difference between both seasons. The temperature data demonstrate that the reservoir is stratified from May to September, the dry season. The water temperature profiles in Alqueva Montante are shown in figure 2. In autumn and winter, all the study locations exhibit isothermal profiles of temperature. Seasonal climate changes, particularly rainfall and solar heating, result in seasonal variations in water balance producing a predictable variation in water level. In the dry season, the water balance is maintained by evaporation. This leads to an increase in salt content, reflected by higher levels of Total Dissolved Solids, Alkalinity, Calcium and Magnesium. Despite this slight increase, water uses were not compromised. As reported by Lory (1995), higher levels of TP and SRP in the wet season reflect the runoff from the catchment area, especially during flood events. In the dry season, nutrient uptake by phytoplankton can deplete Soluble Reactive Phosphorus (Selig *et al.*, 2002), justifying the lower concentrations observed.

Looking for more evidence on both patterns and parameters associated with the temporal variation, we carried out PCA. Tables 2 and 3 summarize the PCA results, including the loadings (participation of the original variables in the new ones). PCA for the wet season renders 6 Principal Components (PC) with eigenvalues higher than 1, accounting for 74 % of total variance. PC1 explains 24 % of the variance, and is contributed by Conductivity, Calcium, Chloride, Magnesium, TDS, Hardness and Alkalinity. Thus, PC1 represents the parameters associated with dissolved salts responsible for mineralization. PC2 explains 15 % of the total variance, with Dissolved Oxy-

Variable **PC 1 PC 2 PC 3 PC 4 PC 5** PC 6 DO mg/L -0.5040.748 0.143 -0.1050.312 0.055 DO % sat -0.5010.720 0.171 -0.0620.330 0.076 pН -0.4830.747 0.068 -0.0490.148 0.046 Т 0.097 0.252 -0.2400.663 0.218 0.120 Conductivity 0.848 0.253 -0.0320.138 -0.0650.026 NO<sub>3</sub> -0.5580.587 -0.0820.016 -0.2940.350 TN -0.3090.345 -0.5760.580 -0.0760.010 0.296 0.325  $NH_4$ 0.207 -0.459 0.493 0.315 SRP 0.107 -0.1740.029 0.295 0.685 0.482 ТР -0.123-0.256-0.027-0.3490.533 -0.294COD 0.345 -0.0340.640 0.235 -0.3450.160 BOD -0.0460.250 0.689 0.256 0.044 -0.158TOC -0.359 0.305 -0.279-0.317 -0.2170.205 POC -0.210-0.2770.622 0.135 -0.2770.350 Ca 0.741 0.418 -0.0180.045 -0.0050.125 Cl 0.634 0.264 -0.2210.147 -0.090-0.088Mg 0.471 -0.168-0.3250.083 0.406 -0.002TDS 0.836 -0.0470.338 -0.0310.022 -0.038TSS 0.158 -0.0230.092 0.385 0.255 -0.719 0.795 Hardness 0.283 -0.179-0.1340.223 -0.117Alkalinity 0.788 0.160 0.003 0.021 0.048 0.062 5.109 2.561 1.879 1.776 1.173 Eigenvalue 3.045 % Variance explained 24.32 14.50 12.19 8.94 8.45 5.58 % Cum. variance 24.32 38.82 51.02 59.96 68.42 74.00

**Table 2.** Loadings of 21 experimental variables on six significant principal components for the wet season. *Pesos de 21 variables experimentales para los 6 componentes principales significativos para la estación húmeda.* 

gen and pH the main participants. PC3 (12.2 % of the variance) represents principally Temperature, BOD, COD and also Nitrate, TN, and TOC. PC4 is highly contributed by POC, Nitrate and Total Nitrogen. PCs 3 and 4 can, then, be related to the input of dissolved and particulate organic matter. PC5 is mainly related to nutrients, while PC6 represents the TSS. The bivariate plot of the loadings of PCs 1 and 2 (Fig. 3) shows that the samples corresponding to the Álamos, Alcarrache, Ardila and Barcas locations appear on the positive side of PC1, due to its higher mineralization. In the negative side, in the third quadrant, appear the samples collect in October, mainly due to high concentrations of TOC, POC and TP. The higher levels of precipitation that occurred may have resulted in the surface runoff of phosphorus and organic compounds from the catchment area, justifying this individualization.

In the dry season, seven principal components

were obtained with eigenvalues > 1, making up 78.6 % of total variance in the dataset; these are shown in Table 3. The first PC accounting for 18.3 % of total variance is correlated primarily with Dissolved Oxygen and pH and secondarily with Temperature, organic variables and SRP, although this last is negatively correlated with the rest. The second PC accounting for 15.14 % of the total variance is correlated with Conductivity, Hardness, TDS and Calcium. The scatter plot of PCs 1 and 2 for the samples shows that all the situations of middle and bottom are located on the positive side of PC1, principally due to the consequences of stratification. In the dry season, surface layers heat up and form a warm layer (epilímnion) overlying cooler, denser water (hipolímnion). In Alqueva Montante (the deepest site), the amplitude between surface and bottom Temperature reached 17 °C. This stratification prevents water mixing and results in the depletion

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**Table 3.** Loadings of 21 experimental variables on seven significant principal components for the dry season. *Pesos de 21 variables experimentales para los siete componentes principales significativos para la estación seca.* 

Variable	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7
DO mg/L	0.747	-0.050	0.383	-0.162	0.181	0.393	0.026
DO % sat	0.688	-0.277	0.393	-0.177	0.206	0.356	0.011
рН	0.855	0.023	0.305	-0.016	-0.057	0.050	-0.011
Т	0.638	-0.235	-0.013	-0.152	0.138	-0.326	0.320
Conductivity	-0.110	0.748	0.349	-0.235	-0.087	-0.239	0.048
NO <sub>3</sub>	-0.079	0.081	<u>0.656</u>	0.663	0.096	-0.154	0.059
TN	-0.020	0.081	0.602	0.720	0.081	-0.116	0.063
NH <sub>4</sub>	-0.345	0.221	-0.463	0.304	<u>0.430</u>	0.064	0.114
SRP	-0.388	0.361	0.264	0.341	0.283	0.116	-0.054
ТР	-0.016	-0.223	-0.223	0.331	0.048	0.117	0.654
COD	0.599	0.316	<u>-0.497</u>	0.204	-0.040	-0.029	-0.165
BOD	0.629	0.510	-0.122	0.254	-0.034	-0.184	-0.059
TOC	0.445	0.017	0.017	0.515	-0.171	0.186	-0.168
POC	0.470	0.132	-0.561	0.207	0.024	-0.225	0.389
Ca	-0.031	0.662	0.267	-0.413	0.337	-0.139	0.252
Cl	0.224	0.485	0.051	-0.190	-0.557	-0.150	0.119
Mg	-0.185	0.247	-0.224	0.223	-0.619	0.509	0.121
TDS	-0.013	0.606	0.117	-0.121	0.052	-0.033	-0.155
TSS	0.333	0.392	-0.505	0.262	0.171	-0.047	-0.364
Hardness	-0.115	0.675	0.145	-0.063	-0.215	0.388	0.269
Alkalinity	-0.014	0.393	-0.286	-0.131	0.610	0.398	0.023
Eigenvalue	3.840	3.180	2.715	2.187	1.678	1.294	1.088
% Variance explained	18.28	15.14	12.92	10.41	7.99	5.94	5.18
% Cum. variance	18.28	33.42	46.35	56.76	64.76	70.71	75.88



**Figure 3.** Distribution of the water samples from the wet season on the plane defined by the first two principal components. *Distribución de las muestras de la estación húmeda en el plano definido por los dos primeros componentes principales.* 

**Table 4.** Loadings of 21 experimental variables on six significant varifactors for the wet season. *Pesos de 21 variables experimentales para 6 seis varifactores significativos para la estación húmeda.* 

Variable	<b>VF 1</b>	<b>VF 2</b>	VF 3	VF 4	VF 5	VF 6
DO mg/L	-0.133	0.960	0.054	0.011	-0.042	-0.028
DO % sat	-0.145	0.944	0.061	0.040	0.009	-0.012
рН	-0.113	0.868	0.170	0.049	-0.149	-0.059
Т	0.074	0.158	-0.110	<u>0.767</u>	-0.002	0.049
Conductivity	0.863	-0.169	0.017	0.180	0.033	0.009
NO <sub>3</sub>	-0.016	0.202	<u>0.896</u>	-0.127	-0.047	0.090
TN	-0.028	0.204	0.901	-0.151	-0.052	0.090
NH <sub>4</sub>	-0.023	-0.235	-0.155	0.140	0.819	0.136
SRP	0.061	0.076	0.040	-0.087	<u>0.901</u>	-0.030
ТР	-0.178	0.075	-0.435	-0.511	0.152	0.249
COD	0.168	-0.214	-0.170	0.790	0.058	0.011
BOD	-0.030	0.312	-0.177	0.596	0.055	0.380
TOC	-0.339	-0.320	0.487	-0.084	0.076	-0.146
POC	-0.329	-0.121	0.150	0.314	0.275	0.637
Ca	0.836	0.047	0.004	0.166	0.036	-0.106
Cl	0.709	-0.125	0.167	0.009	-0.092	0.056
Mg	0.428	-0.222	0.011	-0.381	0.369	0.113
TDS	0.895	-0.046	-0.102	0.063	-0.028	0.001
TSS	0.159	-0.042	0.016	-0.050	-0.022	0.857
Hardness	0.869	-0.009	-0.163	-0.197	0.029	0.054
Alkalinity	0.770	-0.155	-0.116	0.099	0.114	-0.027
Eigenvalue	4.650	3.12	2.27	2.26	1.78	1.44
% Variance explained	22.14	14.87	10.84	10.78	8.49	6.86
% Cum. variance	22.14	37.02	47.86	58.64	67.14	74.00

of hypolimnetic oxygen due to the mineralization of organic matter settled on the bottom (Chapman, 1996). In figure 4, it can be seen that, during the stratified period, the hipolímnion is under anoxic conditions. Notice that, when stratification is disrupted (September-October), the circulation of water tends to mix anoxic water form the bottom through all the vertical profile, lowering surface concentrations of Dissolved Oxygen. This can seriously compromise water uses. Contrary to Boulton & Brock (1999), this period was not followed by an extensive growth of phytoplankton. This is understandable since the processes of internal loading are not expressive due to the youth of the reservoir.

Surface situations in the reservoir and water courses appear on the negative side of PC1, mainly related to low levels of SRP and Ammonia, indicating high levels of nutrient uptake by phytoplankton (Fig. 5). Third and fourth PCs represent the importance of nutrients in total variability (12.9 % and 10.4 % of variance). PCs 5, 6 and 7 explain less than 10 % of variance each.

The values of PCA can be clarified by means of a Varimax rotation of the eigenvalues. By this method, varivalues and varifactors (VFs) are obtained, in which original variables participate more clearly. Table 4 shows the 6 VFs for the wet season spanning the same 74 % of variance. The amount of information explained by VF1 (22.1%) is very similar to PC1 (24.3%), with participation also by Conductivity, Calcium, Chloride, Magnesium, TDS, Hardness and Alkalinity. VF2 (14.9% of variance) accounts for Dissolved Oxygen and pH. VFs 3, 4 and 5 explain the importance of nutrients in the variability of water quality during the wet period (10.8 %, 10.8 % and 8.5 %). These "nutrient" factors represent influences from non-point sources such as agricultural



Figure 4. Dissolved Oxygen (% saturation) profile at Alqueva Montante from March 2003 (1) to January 2004 (11). Oxígeno disuelto (% de saturación) en Alqueva Montante desde Marzo de 2003 (1) a Enero de 2004 (11).

 Table 5.
 Loadings of 21 experimental variables on seven significant varifactors for the dry season. Pesos de 21 variables experimentales para los siete varifactores para la estación seca.

Variable	<b>VF 1</b>	<b>VF 2</b>	VF 3	VF 4	VF 5	VF 6	VF 7
DO mg/L	0.953	0.086	0.045	0.012	0.057	-0.021	-0.012
DO % sat	0.934	-0.041	-0.126	-0.006	0.022	-0.121	-0.011
pH	0.782	0.351	0.078	0.079	-0.272	-0.087	0.032
Т	0.428	0.191	-0.007	-0.154	-0.242	-0.474	0.432
Conductivity	-0.097	0.009	0.863	0.136	-0.110	0.045	-0.167
NO <sub>3</sub>	0.038	-0.071	0.052	0.949	-0.084	-0.047	0.014
TN	0.061	0.004	0.006	0.949	-0.072	-0.005	0.047
NH <sub>4</sub>	-0.458	0.172	-0.033	0.065	0.621	0.013	0.215
SRP	-0.206	-0.095	0.224	0.522	0.392	0.117	-0.149
ТР	-0.050	-0.069	-0.243	0.103	0.124	0.140	0.735
COD	0.121	0.851	-0.011	-0.168	0.034	0.059	0.070
BOD	0.211	0.781	0.294	0.132	-0.092	-0.011	0.082
TOC	0.284	0.475	-0.272	0.322	-0.100	0.247	-0.021
POC	-0.023	0.612	-0.006	-0.175	-0.010	-0.087	0.621
Ca	0.081	-0.096	0.877	-0.019	0.243	-0.180	0.039
Cl	0.030	0.242	0.521	-0.139	-0.482	0.297	0.033
Mg	-0.170	0.082	-0.039	-0.050	-0.079	0.895	0.079
TDS	-0.034	0.181	0.549	0.053	0.117	0.071	-0.258
TSS	-0.094	0.803	-0.002	-0.069	0.270	-0.023	-0.139
Hardness	0.049	-0.026	0.598	0.060	0.139	0.612	0.062
Alkalinity	0.087	0.142	0.234	-0.189	0.816	0.032	0.011
Eigenvalue	3.041	2.925	2.799	2.385	1.804	1.659	1.322
% Variance explained	14.48	13.93	13.32	11.35	8.59	7.90	6.29
% Cum. variance	14.48	28.41	41.74	53.10	61.69	69.59	75.89



**Figure 5.** Distribution of the water samples from the dry season on the plane defined by the first two principal components. *Distribución de las muestras de la estación seca en el plano definido por los dos primeros componentes principales.* 

runoff and atmospheric deposition (Siemenov et al., 2003). The last VF associates TSS and POC, reflecting the importance of particulate organic matter that enters the reservoir during flood events, associated with eroded material. In the dry season the principal sources of variability are different (Table 5). PC1 is broken up by varimax rotation into: (1) VF1, which represents the importance of dissolved oxygen and pH (14.5 %); (2) VF2 accounting for 13.9 % of variance is correlated to COD, BOD, TOC, POC, and TSS. This "organic" factor represents influences from the decomposition of organic matter settled in the anoxic hypolimnion. VF3 can be seen as the mineralization factor, assuming 13.3 % of variance and weighted on Conductivity, Calcium, Chloride and TDS. VFs 4 and 5 show once again the reduced importance of nutrients in the total variability of the data.

Further assessment of temporal changes was evaluated using Discriminant Analysis (DA). For temporal DA we used two classification groups as defined by the seasons (wet and dry). The season was the grouping variable, while the independent variables were all the parameters measured. The stepwise mode, which includes variables step-by-step, beginning with the most significant until no changes are obtained (Pesce & Wunderlin, 2000) gives a Classification Matrix (CM) with 93.2 % right assignations, 89.2 % validated, using only 10 discriminant parameters (Temperature, TDS, Alkalinity, BOD, TP, Conductivity, TSS, DO, COD and Chloride). Figure 6 includes samples of tree patterns that show clear seasonal differences represented in the data. The first pattern accounts for Conductivity, Alkalinity and Chloride, showing higher variability of data in the wet season. The minimum values are due to the dilution effect induced by rain water with low content of dissolved salts. The higher average concentration in the dry season is to be expected due to changes in water balance that cause a concentration effect. All parameters included on VF1 for the wet season tend to show this pattern, suggesting that levels of minerals in the system are seasonal and climate dependent. The second pattern shows higher levels of Temperature during the dry season. BOD and TDS also fit this pattern. The third pattern shows lower average concentrations in the dry season, with respect to Dissolved



**Figure 6.** Patterns observed with temporal variations: (A) dilution (observed during the wet season); (B) Seasonal differences; (C) TP increase (observed during the wet season) and DO decrease, observed during the dry season. *Patrones de variación temporal observados: (A) dilución observada durante la estación húmeda; (B) Diferencias estacionales; (C) Incremento del TP observado durante la estación seca y disminución del OD, observado durante la estación seca.* 

Oxygen and TP. These last two patterns are connected, taking into account that high levels of organic matter (BOD) consume large amounts of oxygen. The decrease of TP during the dry season is expectable due to the reduced presence of eroded material abundant only in flood events.

We carried out spatial DA for both seasons as the next step. An additional problem in spatial DA is to define the number of groups, where each group accounts for a studied area. We found that the best results (in terms of percentage of right assignations from the DF) are obtained when grouping middle and bottom situations. The DA stepwise mode classification matrix for the wet season shows 40.6 % right assignations and only 33.3 % validated, selecting 3 parameters responsible for spatial variations: Dissolved Oxygen, Temperature and Calcium. The low differentiation between areas is expected due to the homogeneity of the water mass, with the expansion of lotic condition in the rainy period (Nogueira, et al., 1999). DA results for the dry season show that only 4 parameters are enough to obtain a good differentiation between the 12 areas (71.3 % right classifications): pH, Temperature, Conductivity and BOD. Figure 7 includes 2 patterns represented in the spatial analysis of the data. The first pattern accounts for high values for BOD, pH and Conductivity upstream in Sr<sup>a</sup> da Ajuda (1), near the border with Spain, often associated with certain effluents (Chapman, 1996). We can observe a



**Figure 7.** Longitudinal and vertical patterns observed in the dry season: (A) important longitudinal differences; (B) expressive depth differences. The light boxes correspond to surface samples while the dark ones correspond to middle and bottom samples. The scale 1 -12 indicates the sample sites, ordered from upstream to downstream. *Patrones longitudinales y verticales observados durante la estación seca: (A) Diferencias horizontales importantes; (B) Diferencias en profundidad. Los rectángulos claros corresponden a muestras superficiales, mientras que los oscuros corresponden a muestras intermedias y profundas. La escala de 1 a 12 indica las estaciones muestreo, ordenadas desde aguas arriba hacia aguas abajo.* 

dilution effect in the transition to the reservoir (1-2). Higher levels appear near the dam in Alqueva Montante (8 e 9). BOD decreases in the discharge section (10), suggesting that the reservoir retains and processes organic matter. The second pattern is associated with the consequences of stratification, expressed by pH and Temperature variation between surface and bottom. High pH values at the surface during the dry season are related to high levels of primary production (Chapman, 1996). Regard that the lowest levels of Temperature registered at Alqueva Jusante (11) indicate a source of thermal pollution, due to the discharge of cold waters made by the dam. Nevertheless, the recovery is rapidly achieved in Barcas (12).

This group of parameters shows a significant

contribution to the variance due to differences between tributary sampling stations, indicating anthropogenic sources of pollution. On the other hand, all the other parameters were demonstrated not to contribute significantly to longitudinal spatial variance, showing that only climate, seasonality and depth are responsible for variations in water quality. Nevertheless, these findings are only valid at the sampling scale used, and for the study period.

### CONCLUSIONS

Environmental analytical chemistry generates multidimensional data that need multivariate statistics to analyse and interpret the underlying information. Pattern recognition techniques pro784

vide different features for the study of spatial and temporal variations in water quality. FA/PCA allows grouping the selected parameters according to common features (mineralization, nutrients, organic). Also, FA/PCA enables the evaluation of the incidence of each of these groups in the overall change in water quality. FA helps to clarify the participation level of each variable in relation to the new ones. Therefore, during the wet season, water quality is primarily controlled by inorganic (mineral) contents explained by VF1 (22.14 % of variance). This nonanthropogenic form of pollution achieves higher concentrations in the tributaries. Dissolved oxygen and pH represent 14.8 % of variance (VF2), followed by VF3 (10.8 % of variance), which represents the high importance of the surface runoff of Nitrate, Phosphorus and particulate organic matter. However in the dry season, the system is mainly controlled by Dissolved Oxygen, pH and Temperature assuming 14.5 % of variance-VF1; VF2 represents the organic parameters (13.3 %); and mineralization is transferred to VF3 (13.3 %). DA affords the better results for both temporal and spatial analysis. It gives an important reduction using only 10 parameters (47.6 % of reduction) to differentiate samples from wet and dry seasons, with 93.2 % right assignations. Box-and-Wisker plots provide a powerful tool for the analysis of patterns, pointing to: (1) the consequences of water balances on ambient salinities; (2) stratification influences; and (3) surface runoff. A spatial approach highlights the upstream source of organic constituents. Additional variability is derived from two important lateral components: the entrance of the Alcarrache stream, bringing waters with low mineralization; and the Degebe River with high levels of BOD. However, in this filling phase, on general parameters, a longitudinal gradient in the lacustrine zone is not evident. The differences tend to appear between lotic and lentic zones. However, the spatial differences noted, can become either more defined during the dry season, or less evident during the expansion of the lotic condition in the rainy period. The reservoir is already controlled by seasonal processes of stratification/mixture determining temporal changes

in the lacustrine zone, and reinforcing the importance of seasonal trend monitoring programmes. Notice that a perspective of watershed-reservoir linkage is critical in order to understand phenomena in the reservoir ecosystem, and to take action to reduce nutrient and organic contaminants. Being an impoundment with multiple uses (irrigation, hydro-power, water supply, recreation), the Alqueva reservoir tends to be subjected to stresses arising from management practices. Therefore, there is a particular need for the managers to understand its physics, chemistry and biology. This knowledge is being achieved through the periodic assessment of water quality. Nevertheless, there is a particular need for further evaluation of the monitoring strategies. One emergent evaluation is the need to refine the temporal and spatial scale in order to better understand the spatial and temporal heterogeneity of water quality. The installation of automatic samplers by EDIA will help to better characterize extreme situations, and provide a warning system for pollution events.

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