TREND STUDY AND ASSESSMENT OF SURFACE WATER QUALITY IN THE EBRO RIVER (SPAIN)

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ABSTRACT

34 Physical-chemical and chemical variables were analysed in surface water samples collected every month over a period of twenty-four years. They were determined from thirteen sampling stations located along the Spanish Ebro River affected by anthropogenic and seasonal influences. The trend study was performed using the Mann-Kendall Seasonal Test and the Sen´s Slope estimator. Results revealed parameter variation over time due mainly to the reduction in phosphate concentration and increasing pH levels at the Ebro Basin during the 1981-2004 period. Exploratory analysis of data was also carried out by display methods (cluster analysis), and unsupervised pattern recognition (principal component analysis) in an attempt to differentiate between sources of variation in the water quality. PCA has allowed the identification of the following factors: geologic, climatic and anthropogenic. Spatial and seasonal sources of variation were identified that affect the quality and hydrochemistry of river water.

Key words: Mann-Kendall, Sen´s slope, water quality, surface water, hydrochemistry, principal component analysis, cluster analysis.

1.   Introduction

Sampling networks for monitoring the water quality of rivers constitute a great source of data for obtaining a local and temporal vision of the river state. In addition, a wide network gives an insight into the evolution of the ecosystem over time. This gives a better knowledge of its temporal state with regards to future evolution and forecasts if the number of variables analysed is extensive enough given that the study of seasonal or geographical evolution is quite complex (Simeonova, P. et al., 2003; Simeonov, V., 2002). Furthermore, challenging information is difficult for the public to digest and would require interpretation and/or simplification to be useful.

The European Union has established a framework for water policies. The European Directive 2000/60/EC urges its members to conclude periodical trend studies of different water pollutants (Annexe V Section 2.4.4). This document considers the term "trend" as the monotonic variation of the pollutant concentration with regard to time.

Observational and historical environmental time-series data are generally used for planning and designing environmental projects. There are a lot of statistical tools for trend and seasonal variations assessment (Wei, 2005; Shumway & Stoffer, 2006), but the procedure for calculating the trends has been widely discussed by the scientific community. There exist two groups of mathematical tools to calculate these trends (Zhang et al., 2006; Kundzewicz & Robson, 2004). The parametric method, based principally in linear and residual models, and the non-parametric method, such as the Mann-Kendall's Test (Mann (1945), Kendall (1975)) and the Sen's slope estimator (Sen (1968)).

The parametric methods, what are more powerful than non-parametric ones, but they require the data be independent and normally distributed, examine the linearity of the regressions (Montgomery (1982)), using the t test to calculate the significance of slope (Snedecor and Cochran (1980)). In the cases of data set with a seasonal component or with variables correlated, these techniques show false

positives. The majority of non-parametric methods are based on the Mann-Kendall's Test (MK), which assumes the observations are independent. The application of Mann-Kendall's Test for an **n** independent series and data (x_1, x_2, ..., x_n) being identically distributed suggests the previous acceptance of the null hypothesis **H_0** (non existence of trend). However this does not apply to information that presents a seasonal component, such as the information of water quality. In 1982 Hirsch et al. developed a modification of the MK test, the Mann-Kendall's Seasonal Test (SMK). It consists of the sum of the individual MK's values for each cyclic period, thereby removing the seasonal component.

Using the Mann-Kendall's Test it is possible to determine the existence of an increasing or decreasing trend, but it is hard to measure if the method, Sen's Slope Estimator developed by Sen (1968), allows the calculation of the slope of the regression line for each parameter over any time without the influence of outliers (Bouza-Deaño et al. 1999).

In order to apply and check the use of non-parametric statistical methods, the aim of the present study consists of the detection and quantification of the water quality trends in a Spanish River using both the Mann-Kendall Seasonal Test and the Sen's Slope Estimator. The objective is to obtain a deeper understanding of the evolution in water quality through the years.

2. Methods

2.1. Monitoring area

The Ebro River (Figure 1) Map showing the water quality monitoring sites on the Ebro River) is the largest River of the Iberian Peninsula. It originates from a natural reservoir in a forested area (elevation about 1200 m) near the town of Fontibre in Cantabria, Spain, and it flows into the Ebro Delta (outlet). The river flows from the North Eastern peninsula and traverses 800 Km before terminating in the Mediterranean Sea. The river drains a catchment area of about 85924 km^2. Segre,

Cinca, Aragón, Gallego and Zadorra are the main tributaries of the Ebro River. Zaragoza (population about 650000), Vitoria (population about 225000), Pamplona (population about 190000), Logroño (population about 145000), Lérida (population about 125000) and Huesca (population about 48000) are the major urban settlements on the banks of the river.

The river is usually used as a supply of water for agriculture, cattle breeding (89.3%), domestic (7.2%) and industrial activities (3.5%) from a total supply of 18217 Hm^3/year in 2004. In addition, the river receives domestic and industrial wastewater from numerous minor settlements along the bed. Discharges into the Ebro River vary at different locations, showing an increase downstream, probably due to inputs from the tributaries or natural recharge of the stream. The drainage of the Ebro basin extends over the NW-SE direction with similar climatic conditions throughout. During the summer months, the maximum annual temperature is up to 34ºC and during the winter months the minimum temperature drops to -5ºC.

In the present study, a total of 13 sampling sites were selected. They correspond to sampling stations from the National Water Quality Control Network (ICA Network) directed by Spanish Government for the Ebro River (Spanish Ministry of the Environment). The sampling sites were the following: Cereceda (Site-1), Miranda (Site-2), Conchas de Haro (Site-3), Mendavia (Site-4), Castrón (Site-5), Pignatelli (Site-6), Zaragoza (Site-7), Presa Pina (Site-8), Sastago (Site-9), Mequinenza (Site-10), Ribarroja (Site-11), Ascó (Site-12) and Tortosa (Site-13). The first three sites (1-5) are located in low pollution regions with a low population density. Another six sites (6-9) are located in high pollution zones and are affected due to domestic drains and emptying of polluted tributaries into the river at this stretch. The last four sites (10-13) are in a downstream region with moderate pollution.

2.2. Monitored pollutants and analytical methods

The data used in this study is part of the database maintained by the Spanish Ministry of the Environment. This monitoring network and sampling strategy was

designed to cover a wide range of pollutants. The monitoring program collects samples each month at the thirteen sampling stations. With this frequency we can monitor changes caused by the seasonal hydrological cycle over a 24 year period (1981-2004). The network provides enough data (3620 samples, due to 124 samples could not be sampling by different circumstances) to determine the quality of the river system, including tributaries and pollutants that have an impact on downstream.

Preservation and transportation of samples to the laboratory were in accordance with standard method (APHA, 1992). Water temperature, Air temperature, Flow rate and Dissolved oxygen were measured *in situ*. The other parameters were analysed in the Central Laboratory of the Ebro Basin Authority (Confederación Hidrográfica del Ebro, Zaragoza, Spain) following the standard protocols (APHA, 1992). The quality of analytical data during the last years was ensured by using the UNE-EN-ISO 17025 Norm and Accreditation of the Central Laboratory. During the previous years it followed Good Laboratory Practices, such as standard protocols, blank measurements, spiked and duplicate samples. The laboratory regularly participates in international programs on quality control. The samples were analysed for 34 parameters listed in Table 1.

Table 1. Physico-chemical parameters determined and analytical techniques used in the study.

Variable	Abbreviation	Analytical technique	Units
Total alkalinity	T-ALK	Titration	mgl^{-1}
Arsenic	AS	ICP-OES	μgl^{-1}
Calcium	CA	ICP-OES	mgl^{-1}
Water flow	FLOW	Area-velocity	$m^3 day^{-1}$
Cadmium	CD	ICP-OES	mgl^{-1}
Chloride	CL	Titration	mgl^{-1}
Cyanide	CN	Spectrophotometry	μgl^{-1}
Total coliform	T-COLI	MPN method	MPN/100 ml
Electrical conductivity	EC	Conductometry	μScm^{-1} at 20ºC
Total chromium	T-CR	ICP-OES	μgl^{-1}
Copper	CU	ICP-OES	μgl^{-1}
5-days biochemical oxygen demand	BOD	Potentiometry/DO probe	mgl^{-1}
Tensioactives	TEN	Spectrophotometry	μgl^{-1}
Chemical oxygen demand	COD	Redox titrometry (K_2CrO_4)	mgl^{-1}
Iron	FE	ICP-OES	μgl^{-1}
Phenols	PHE	Spectrophotometry	μgl^{-1}
Fluor	F	Ion selective electrode	μgl^{-1}
Mercury	HG	ICP-OES	μgl^{-1}
Dissolved hydrocarbons	D-HID	Spectrophotometry	mgl^{-1}
Potassium	K	ICP-OES	mgl^{-1}
Total suspended solids	TSS	Filtration/drying at 105ºC/weighing	mgl^{-1}
Magnesium	MG	ICP-OES	μgl^{-1}
Manganese	MN	ICP-OES	mgl^{-1}
Sodium	NA	ICP-OES	mgl^{-1}
Ammonium	NH4	Spectrophotometry	mgl^{-1}
Nitrate	NO3	Spectrophotometry	mgl^{-1}
Dissolved oxygen	DO	Potencipometry/DO probe	mgl^{-1}
Lead	PB	ICP-OES	μgl^{-1}
pH	PH	Potenciometry/pH probe	pH units
Phosphate	PO4	Spectrophotometry	mgl^{-1}
Sulphate	SO4	Spectrophotometry	mgl^{-1}
Water temperature	W-TEMP	Temperature probe	ºC
Air temperature	A-TEMP	Temperature probe	ºC
Zinc	ZN	ICP-OES	μgl^{-1}

The Water quality index (WQI) was also calculated. It was adopted by the Spanish Government in 1983 (Ministerio de Obras Públicas y Urbanismo, 1983) and based on the development by Provencher and Lamontagne from the Water Quality Service on the Canadian Ministry of Natural Resources (Natural Resources Canada, NRCan) (Provencher and Lamontagne, 1977). The WQI index uses 23 physical, chemical and physico-chemical parameters to obtain a numerical indicator from 0 (poor water quality) to 100 (high water quality).

2.3. Statistical data treatment and trend study

2.3.1. Parametric statistical tools

The Pearson product-moment coefficient (PPMC) was the first parametric statistical technique applied to the data set. This univariate tool assumes that the two variables are measured on at least interval scales, and determines the extent to which values of the two variables are "proportional" to each other. To interpret the coefficients correlation, a common source must be assigned to the correlated variables with regard to the main sources of this River. Linearity was also verified by graphical examination. This procedure consisted of verifying the linearity and observing the linear profile of the points (the pairs of data x-y). Sometimes a false linearity is due to an accumulation of points plus an outlier.

Additionally, cluster Analysis (CA) was the unsupervised multivariate technique used to classify the objects into categories or clusters based on their nearness or similarity (Vega et al., 1998). It is the most common approach in which clusters are formed sequentially by starting with the most similar pair of objects and forming higher clusters step by step (Otto, 1998). Cluster analysis was applied to the data set with the aim of grouping similar sampling sites (spatial variability) and spreading them over the river (dendrogram). Hierarchical agglomerative clustering was performed on the normalised data by means of the Ward's method and using Euclidean distances (D_{link}/D_{max}) (Wunderlin et al., 2001; Simeonov et al., 2003).

Principal Components Analysis (PCA) was performed on the rearranged data matrix, so that it explained the structure of the underlying data set (Liu et al., 2003). PCA is a widely used tool in science and engineering. We performed the PCA with a Varimax rotation, extracting the factors or PCs, which explain more than 4 – 6 % of the total variance of the data set, and also more than 40 % of accumulated variance. Kaiser criterion was also used (eigenvalue >1). Experimental data was standardised in order to avoid misclassification due to wide differences in data dimensionality (Liu et al., 2003). Standardisation tends to increase the influence of small variance and reduce the influence of large ones. Furthermore, the standardisation procedure eliminates the influence of different units of measurement and renders the data dimensionless.

Consequently, multivariate analysis of the data was performed through CA and PCA (Wunderlin et al., 2001; Simeonov et al., 2003). All mathematical and statistical computations were made using Excel 2003 (Microsoft, 2003) and STATISTICA 6.0 (StatSoft, Inc, USA, 2001) software.

2.3.2. Non-parametric statistical tools

Spearman´s R test (ρ) is a non-parametric measure of correlation, which assesses how well an arbitrary monotonic function can describe the relationship between two variables without making any assumptions about the frequency distribution of the variables. ρ is simply a special case of the Pearson product-moment coefficient in which the data is converted to ranks before calculating the coefficient. The raw scores are converted to ranks, and the differences D between the ranks of each observation on the two variables are calculated. ρ is then given by:

$$\rho = \frac{\sum_{i=1}^{n} R(x_i)R(y_i) - n\left(\frac{n+1}{2}\right)^2}{\left(\sum_{i=1}^{n} R(x_i)^2 - n\left(\frac{n+1}{2}\right)^2\right)^{0.5}\left(\sum_{i=1}^{n} R(y_i)^2 - n\left(\frac{n+1}{2}\right)^2\right)^{0.5}}$$

Where R(x) and R(y) are ranks of a pair of variables (x and y) each containing n observations.

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The non-parametric MK statistical test (Mann, 1945; Kendall, 1975) has usually been used to assess the significance of a trend at a site. The MK statistic S is defined as follows:

$$S = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \text{sgn}(X_o - X_i)$$

Where X_o are the sequential data values, n is the length of the data set, and

$$\text{sgn}(\theta) = \begin{cases} 1 & for & \theta > 0 \\ 0 & for & \theta = 0 \\ -1 & for & \theta < 0 \end{cases}$$

Mann (1945) and Kendall (1975) documented that, when n≥8, the statistic S is approximately normally distributed with the mean and the variance given by:

$$E[S] = 0$$

$$Var(S) = \frac{n(n-1)(2n+5) - \sum_{i=1}^{n} t_i i(i-1)(2i+5)}{18}$$

Where t_i is the number of ties of extent i. The standardised test statistic Z is computed by:

$$Z = \begin{cases} \dfrac{S-1}{\sqrt{Var(S)}} & for & S > 0 \\\\ 0 & for & S = 0 \\\\ \dfrac{S+1}{\sqrt{Var(S)}} & for & S < 0 \end{cases}$$

The standardised MK statistic Z follows a standard normal distribution with mean

of zero and variance of one under the null hypothesis of no trend. A positive Z value indicates an upward trend, whereas a negative one indicates a downward trend. The p value (probability value p) of the MK statistic S of sample data can be estimated using the normal cumulative distribution function:

$$p = 0.5 - \Phi(|Z|)$$

Where

$$\Phi(|Z|) = \frac{1}{2\pi} \int_0^{|Z|} e^{-\frac{t^2}{2}} dt$$

If the p value is small enough, the trend is quite unlikely to be caused by random sampling. At the significance level of 0.05, if p≤0.05, then the existing trend is assessed to be statistically significant.

If a linear trend is present, the true slope may be estimated by (a) computing the least squares estimate of the slope or (b) by linear regression methods. However b can deviate greatly from the true slope if there are gross errors or outliers in the data set. Sen (1986) developed a procedure as an extension of a test by Theil (1950), called Sen´s method, which is not greatly affected by gross data errors or outliers, and it can be computed when data is missing. This test is closely related to the Mann-Kendall test (Gilbert, 1987).

In order to obtain the Sen´s slope estimator it is necessary first to compute the N´ slope estimates, Q, as:

$$Q = \frac{x_{i'} - x_i}{i' - i}$$

Where $x_{i'}$ and x_i are data values at times i´ and i respectively, and where i´>i; N´ are the number of data pairs for which i´>i. The median of these N´ values of Q is Sen´s estimator of slope. If there are only one datum in each time period, then

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$$N' = \frac{n(n-1)}{2}$$

3. Results and discussion

Water-quality monitoring of the Ebro River was regularly conducted over a period of 24-years (1981-2004) at thirteen different sites. All the samples were analysed for thirty four parameters. The basic statistics for the 24-years of data set are summarised in Table 2.

Table 2. Mean values with standard deviation of different water-quality parameters at different sites on the Ebro River during 1981-2004.

Parameter	SITE-1	SITE-2	SITE-3	SITE-4	SITE-5	SITE-6	SITE-7
T-ALK	139.5 ± 44.8	148.9 ± 31.5	158.5 ± 27.9	153.1 ± 17.9	172.3 ± 18.1	177.5 ± 20.1	200.3 ± 29.1
AS	0.6 ± 2.0	0.4 ± 2.1	0.5 ± 1.2	0.9 ± 3.1	0.6 ± 2.0	0.4 ± 1.8	0.6 ± 3.8
CA	56.6 ± 15.4	67.0 ± 16.9	71.4 ± 13.9	79.0 ± 12.7	87.0 ± 12.9	92.7 ± 15.6	121.1 ± 35.0
FLOW	45.0 ± 65.04	50.5 ± 84.31	73.6 ± 124.27	96.0 ± 98.80	179.9 ± 215.22	157.3 ± 178.30	178.9 ± 189.96
CD	0.0 ± 8.4E-05	0.0 ± 2.5E-04	0.0 ± 2.6E-04	0.0 ± 1.1E-03	0.0 ± 1.1E-03	0.0 ± 2.4E-04	0.0 ± 1.6E-04
CL	12.0 ± 4.2	39.1 ± 19.1	43.1 ± 20.4	78.0 ± 32.5	96.6 ± 47.8	115.7 ± 56.3	173.1 ± 100.3
CN	1.0 ± 1.9	5.6 ± 20.5	6.1 ± 12.2	3.1 ± 6.0	4.0 ± 15.2	1.9 ± 7.0	1.4 ± 3.4
T-COLI	2805 ± 5801	7920 ± 20902	15323 ± 19205	26260 ± 56257	58193 ± 177507	27013 ± 75081	33033 ± 79158
EC	320 ± 65	470 ± 121	496 ± 115	648 ± 155	759 ± 226	829 ± 261	1160 ± 498
T-CR	0.3 ± 0.6	1.3 ± 4.8	1.4 ± 3.7	1.4 ± 4.0	2.0 ± 5.4	1.3 ± 4.3	1.5 ± 4.5
CU	2.0 ± 3.7	2.7 ± 4.4	2.4 ± 2.8	2.9 ± 4.0	2.4 ± 4.2	4.1 ± 13.9	3.7 ± 6.2
BOD	3.8 ± 2.8	5.2 ± 4.7	9.4 ± 7.0	7.0 ± 7.9	5.3 ± 3.6	6.2 ± 5.9	7.2 ± 5.1
TEN	57.0 ± 123.3	50.1 ± 94.5	55.2 ± 60.7	63.6 ± 73.2	48.2 ± 56.0	36.9 ± 44.2	36.8 ± 43.6
COD	11.2 ± 4.3	16.7 ± 4.7	18.9 ± 3.9	15.7 ± 3.9	13.9 ± 4.0	14.3 ± 3.2	14.4 ± 4.0
FE	75.4 ± 64.9	61.7 ± 61.3	73.6 ± 63.5	101.0 ± 98.3	100.8 ± 141.2	105.7 ± 124.7	140.4 ± 188.5
PHE	0.7 ± 2.7	1.8 ± 4.9	5.4 ± 6.7	2.0 ± 2.4	1.6 ± 2.5	1.6 ± 2.7	1.5 ± 2.4
F	72.1 ± 50.7	83.1 ± 47.2	113.3 ± 39.4	111.6 ± 40.9	105.0 ± 40.7	120.6 ± 48.8	178.2 ± 105.6
HG	0.1 ± 0.2	0.2 ± 3.3	0.0 ± 0.1	0.1 ± 0.3	0.0 ± 0.1	0.0 ± 0.4	0.0 ± 0.1
D-HID	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.2	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
WQI	84.2 ± 7.6	71.1 ± 6.7	73.1 ± 8.6	69.9 ± 6.6	72.9 ± 8.5	64.2 ± 6.5	60.2 ± 7.9
K	1.5 ± 0.5	1.8 ± 0.6	2.4 ± 0.8	2.9 ± 1.0	3.5 ± 1.7	3.5 ± 1.4	3.9 ± 1.6
TSS	9.6 ± 18.9	9.7 ± 18.1	12.7 ± 39.2	34.4 ± 80.3	38.2 ± 105.4	78.0 ± 502.5	75.7 ± 149.0
MG	8.4 ± 4.1	9.2 ± 3.8	9.6 ± 3.7	11.2 ± 4.0	14.4 ± 7.5	16.7 ± 6.5	26.3 ± 12.7
MN	22.9 ± 19.5	10.8 ± 10.2	13.7 ± 11.1	21.7 ± 15.6	21.5 ± 30.3	21.3 ± 26.8	24.3 ± 29.6
NA	6.0 ± 1.9	29.6 ± 15.6	33.5 ± 17.6	58.3 ± 25.4	67.8 ± 33.8	81.7 ± 39.5	123.9 ± 73.5
NH4	0.1 ± 0.2	0.2 ± 0.3	0.6 ± 0.9	0.2 ± 0.4	0.2 ± 0.2	0.2 ± 0.2	0.2 ± 0.2
NO3	4.4 ± 3.3	7.4 ± 5.2	9.2 ± 4.9	10.4 ± 4.3	11.4 ± 3.9	12.5 ± 3.9	19.0 ± 7.7
DO	9.9 ± 1.4	9.0 ± 1.8	7.7 ± 2.2	9.1 ± 1.6	9.1 ± 1.7	9.8 ± 1.7	10.0 ± 1.9
PB	1.3 ± 2.9	1.2 ± 5.3	2.3 ± 2.7	1.8 ± 4.2	1.5 ± 4.7	1.9 ± 5.1	3.0 ± 8.5
pH	8.0 ± 0.3	7.9 ± 0.3	7.8 ± 0.3	7.9 ± 0.3	7.9 ± 0.3	7.9 ± 0.3	7.9 ± 0.2
PO4	0.2 ± 0.3	0.2 ± 0.2	0.6 ± 1.2	0.7 ± 0.5	0.5 ± 0.5	0.5 ± 0.6	0.4 ± 0.4
SO4	25.2 ± 8.2	57.5 ± 23.5	62.9 ± 24.0	95.3 ± 32.5	105.2 ± 44.4	120.7 ± 48.3	218.8 ± 122.1
W-TEMP	12.8 ± 5.2	15.6 ± 5.5	15.0 ± 5.5	14.3 ± 5.7	14.0 ± 5.7	14.5 ± 6.1	15.0 ± 6.2
A-TEMP	14.3 ± 7.6	14.9 ± 7.0	14.3 ± 6.5	14.6 ± 6.3	15.5 ± 7.2	15.7 ± 7.3	16.9 ± 8.1
ZINC	19.6 ± 29.7	35.5 ± 46.5	33.2 ± 32.4	36.6 ± 33.1	36.1 ± 42.9	38.1 ± 44.7	43.0 ± 48.2

Parameter	SITE-8	SITE-9	SITE-10	SITE-11	SITE-12	SITE-13
T-ALK	200.7 ± 28.4	187.7 ± 64.6	160.7 ± 21.4	160.4 ± 14.7	160.7 ± 12.8	164.7 ± 13.8
AS	3.5 ± 38.3	0.9 ± 3.5	1.8 ± 8.5	4.1 ± 15.7	0.7 ± 3.1	0.6 ± 2.3
CA	133.8 ± 41.2	137.8 ± 41.1	106.9 ± 25.4	97.3 ± 16.2	104.2 ± 17.3	104.8 ± 16.9
FLOW	72.8 ± 20.07	191.3 ± 225.80	201.5 ± 170.33	295.8 ± 196.52	358.7 ± 249.44	268.8 ± 229.49
CD	0.0 ± 4.2E-04	0.0 ± 2.7E-04	0.0 ± 2.2E-04	0.0 ± 2.6E-04	0.0 ± 3.2E-04	0.0 ± 4.2E-04
CL	184.6 ± 100.4	220.9 ± 114.0	116.0 ± 62.8	95.6 ± 40.9	116.5 ± 43.3	117.1 ± 43.8
CN	3.7 ± 10.2	2.3 ± 5.0	4.0 ± 10.4	4.6 ± 18.7	2.3 ± 13.3	1.2 ± 2.3
T-COLI	61933 ± 90668	15385 ± 26032	1339 ± 4673	3918 ± 14197	14220 ± 47855	51332 ± 138502
EC	1266 ± 520	1333 ± 550	966 ± 337	870 ± 246	907 ± 236	917 ± 236
T-CR	2.1 ± 8.6	1.1 ± 2.4	1.0 ± 2.8	2.7 ± 6.5	1.1 ± 3.1	2.1 ± 5.5
CU	2.8 ± 5.0	4.8 ± 8.0	2.1 ± 3.5	2.3 ± 3.7	2.8 ± 5.3	3.5 ± 5.3
BOD	12.3 ± 9.3	9.7 ± 7.5	4.5 ± 3.1	4.1 ± 2.7	4.0 ± 2.3	4.6 ± 4.0
TEN	80.0 ± 91.6	46.2 ± 50.7	44.0 ± 68.9	40.4 ± 57.4	43.6 ± 117.1	53.1 ± 166.3
COD	16.2 ± 5.6	15.1 ± 3.4	10.5 ± 2.0	9.5 ± 2.0	9.7 ± 1.9	9.4 ± 1.7
FE	121.9 ± 134.5	95.5 ± 78.3	32.8 ± 35.2	45.6 ± 35.5	50.1 ± 52.1	56.4 ± 50.9
PHE	5.4 ± 6.7	4.1 ± 6.0	1.2 ± 3.0	1.0 ± 3.1	1.5 ± 2.4	1.2 ± 2.4
F	176.5 ± 69.3	192.7 ± 69.4	158.8 ± 72.3	157.1 ± 61.0	218.7 ± 76.0	214.5 ± 57.8
HG	0.1 ± 0.7	0.0 ± 0.0	0.0 ± 0.1	0.0 ± 0.1	0.0 ± 0.1	0.1 ± 0.5
D-HID	0.1 ± 0.2	0.1 ± 0.2	0.1 ± 0.3	0.1 ± 0.2	0.1 ± 0.3	0.1 ± 0.1
WQI	59.1 ± 9.4	64.9 ± 9.4	74.0 ± 7.9	74.3 ± 7.2	68.5 ± 5.7	68.3 ± 7.0
K	4.7 ± 2.5	4.7 ± 1.7	3.8 ± 1.2	3.2 ± 0.8	3.4 ± 0.9	3.5 ± 1.0
TSS	80.6 ± 273.5	65.6 ± 321.0	6.4 ± 8.1	7.4 ± 5.9	11.0 ± 10.8	10.4 ± 10.4
MG	26.0 ± 12.0	33.0 ± 15.8	23.1 ± 9.8	22.0 ± 7.6	22.0 ± 7.0	23.3 ± 7.1
MN	21.6 ± 21.0	24.3 ± 15.9	24.0 ± 35.6	14.8 ± 15.5	15.3 ± 15.7	18.7 ± 41.4
NA	131.5 ± 74.2	152.7 ± 88.1	90.3 ± 44.4	74.3 ± 27.6	80.7 ± 29.5	82.0 ± 29.5
NH4	0.6 ± 0.7	0.2 ± 0.2	0.3 ± 0.4	0.2 ± 0.2	0.2 ± 0.3	0.3 ± 1.1
NO3	17.5 ± 6.9	15.0 ± 5.2	10.5 ± 3.9	9.3 ± 3.0	9.9 ± 3.1	10.3 ± 3.1
DO	8.1 ± 2.9	10.9 ± 2.8	8.0 ± 2.9	7.5 ± 2.7	9.4 ± 1.8	9.5 ± 1.4
PB	3.3 ± 7.2	5.2 ± 11.8	3.6 ± 9.7	2.4 ± 6.2	2.6 ± 7.3	2.7 ± 6.1
PH	7.8 ± 0.3	8.0 ± 0.3	7.8 ± 0.3	7.8 ± 0.3	7.9 ± 0.3	8.0 ± 0.2
PO4	0.9 ± 0.8	0.4 ± 0.4	0.2 ± 0.2	0.3 ± 0.2	0.5 ± 0.4	0.5 ± 0.4
SO4	246.7 ± 129.8	318.5 ± 171.9	198.1 ± 94.4	172.2 ± 65.3	188.9 ± 66.6	193.4 ± 64.8
W-TEMP	15.3 ± 6.3	16.2 ± 7.0	15.7 ± 5.8	15.3 ± 5.4	16.9 ± 6.2	17.4 ± 5.8
A-TEMP	17.9 ± 8.7	17.9 ± 8.6	17.8 ± 8.7	19.1 ± 8.2	19.8 ± 8.1	20.7 ± 7.2
ZINC	48.5 ± 53.2	34.9 ± 41.6	29.1 ± 28.3	42.1 ± 87.7	31.2 ± 34.3	30.1 ± 32.8

3.1. Correlations study

The correlation matrix of the 34 variables was calculated (Pearson). Because the 13 sampling sites were combined to calculate the correlation matrix, the correlation coefficients should be interpreted with caution as they are affected simultaneously by spatial and temporal variations. Nevertheless, some clear hydrochemical relationships can be readily inferred: High and positive correlation can be observed between alkalinity, sodium, potassium, calcium, magnesium, chloride, nitrate, sulphate and electrical conductivity (r=0.55 to 0.96). These parameters are indicative of the water mineralization. Flow rate is negatively correlated to most variables, since an increase in flow rate causes dilution of concentrations. Fe, Mn and TSS are positively correlated between them.

Temporal variations of the water-quality parameters (Table 2) were evaluated through a season-parameter correlation matrix (Spearman´s R test). This showed that the majority of parameters were found to be significantly ($p<0.05$) correlated with the month of the year, except T-ALK, CD, CR-TOT, TEN, FE, PHE, HG, D-HIDS, NH4 and ZN. Among these, Temperature exhibited the highest correlation coefficient (R=0.41). Other parameters exhibiting high correlation were DO (R=-0.43), K (R=0.36), NA (R=0.35), CL (R=0.31), FLOW (R=-0.27), EC (R=0.25), SO4 (R=0.25), MG (R=0.23). A graphical example is show in Figure 2 (Monthly DO variation in Site-1).

These season-correlated parameters can be viewed as representing the major source of temporal variations in water quality. According to the pollution sources mentioned above, these correlations can be explained on the basis of seasonal features in the monitored river areas. Wide seasonal variations in temperature and river discharge year round can be attributed to the high seasonality in various water-quality parameters. The non-significant correlation of BOD, DQO, NH4 and TEN with season indicates a contribution of the anthropogenic sources in the catchments.

3.2. Multivariate statistical analysis

3.2.1. Cluster analysis

The water-quality data (3620 observations) was further subjected to different multivariate statistical techniques to explore their temporal and spatial trends

Cluster analysis rendered a dendrogram (Figure 3. Dendrogram showing clustering of sampling on the Ebro River) where all thirteen sampling sites of the river were grouped into three statistically significant clusters at (D_{link}/D_{max})x100 < 70%. The clustering procedure highlighted two groups of sites in a very convincing way because the sites in these groups have similar characteristics and natural source types. Cluster I (Sites 1-5), cluster II (Sites 6-9) and cluster III (Sites 10-13) correspond to highest water quality sites (clusters I and III) and lowest water quality sites (cluster II). This implies that for rapid assessment of water quality, only one site in each cluster may be an accurate assessment of the water quality for the whole network.

This classification is coincidental with the WQI medium values in each sampling site as shown in Table 2, where sampling sites 6, 7, 8 and 9 have the lowest values.

It is evident that the CA technique is useful in offering reliable classification of surface waters in the whole region and will make it possible to design a future spatial sampling strategy in an optimal manner. Thus, the number of sampling sites in the monitored network was reduced; and therefore cost, without loosing any value to the outcome. There are other reports (Wunderling et al.. 2001; Simeonov et al. 2003) where this approach was successfully applied in water-programs.

3.2.2. Principal Components Analysis

The Screen plot was used to identify the number of PCs to be retained in order to comprehend the underlying data structure (Jackson, 1991; Vega et al. 1998). In the present study, the Screen plot showed a pronounced change of slope after the four eigenvalues. Rotation of the axis defined by PCA produced a new set of factors, or PCs.

1 Each PC involves a subset of the original variables divided into groups. Thus, PCA result

2 from the present data set minimised the contribution of less significant variables. The

3 Varimax rotation reduces all of the variables to four different PCs, which explains more

4 than 80% of the total variance (Table 3). Variables with communalities lower than 0,5 were

5 removed due to it low significance.

6

Table 3. Loadings of experimental significative variables (18) on the first four rotated PCs for complete data set.

PARAMETER	PC1	PC2	PC3	PC4
T-ALK	<u>0,720</u>	0,160	-0,448	0,010
CA	**0,966**	0,004	-0,058	-0,064
CL	**0,946**	0,081	0,190	0,032
EC	**0,957**	0,062	0,122	-0,011
BOD	0,016	0,300	0,051	**0,761**
COD	-0,225	<u>0,529</u>	-0,121	<u>0,620</u>
FE	0,023	**0,878**	-0,059	0,060
F	<u>0,575</u>	-0,060	0,205	-0,217
K	**0,824**	0,041	0,178	0,098
TSS	0,094	**0,922**	-0,050	0,024
MG	**0,951**	-0,005	0,187	-0,103
MN	0,131	**0,874**	0,133	0,105
NA	**0,923**	0,076	0,190	0,075
NH4	0,067	-0,157	-0,077	<u>0,743</u>
NO3	**0,760**	0,169	-0,453	-0,030
SO4	**0,940**	-0,044	0,218	-0,043
W-TEM	0,239	0,008	**0,902**	0,013
A-TEM	0,262	0,026	**0,856**	-0,087
Eigenvalue	7,888	3,147	2,061	1,324
%Total Variance	43,82	17,48	11,45	7,35
%Variance	43,82	61,30	72,75	80,10

Tendrías que decir en algún lado qué significan las negritas y los subrayados o ponerlas todas en negrita ya que son todas mayores de 0.75 como dices aquí abajo

Liu et al. (2003) classified the factor loadings as 'strong', 'moderate', and 'weak' corresponding to absolute loading values of > 0.75 (bold values in Table 3), 0.75-0.50 (cursive values in Table 3) and 0.50-0.30. respectively.

PC1 explains 43,8% of total variance and has strong positive loadings for total calcium, conductivity, magnesium, chloride, sulphate, sodium, potassium and nitrate. This can be attributed to a mineral component of the river water and could be conditionally named the "geogenic" factor. PC2 (17,5% of total variance), with high correlation of suspended solids, iron and manganese, is the "turbidity" factor. PC3 (11.4%) has a strong positive loading for water and air temperature, so it could be conditionally named the "climatic" factor. PC4 (7,4%) explain only biological oxygen demand, ammonium and chemical oxygen demand and could be conditionally named an "anthropogenic" factor.

3.3. Trend analysis

The Mann-Kendall Seasonal Test was applied in order to study trends of water quality parameters for 24 years (1981-2004). In the cases in which a trend was detected (positive or negative) quantified levels of the above mentioned trend were found by means of Sen's slope. The results of the trends study are shown in Table 4. In 16% of the cases the counterfoil information did not contain sufficient information to help the analysis of non - parametric trends.

Table 4. Results of the Sen's Slope Test (n.t. = "not trend", - = "not data enough").

PARAMETER	SITE												
	1	2	3	4	5	6	7	8	9	10	11	12	13
T-ALK	n.t.	1.06	n.t.	n.t.	n.t.	n.t.	0.31	n.t.	n.t.	n.t.	n.t.	0.50	n.t.
AS	-	<1E-5	<1E-5	-	-	<1E-5	<1E-5	<1E-5	-	-	-	<1E-5	<1E-5
CA	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.
FLOW	n.t.	n.t.	n.t.	-0.89	n.t.	n.t.	n.t.	-	n.t.	n.t.	n.t.	n.t.	n.t.
CD	-	<1E-5	-	-	-	0.0007	0.0010	0.0030	-	-	-	0.0125	0.0068
CL	-0.4	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.
CN	-	<1E-5	0.17961	<1E-5	<1E-5	<1E-5	<1E-5	0.12981	-	<1E-5	<1E-5	<1E-5	<1E-5
T-COLI	-100	-134	-424	n.t.	n.t.	n.t.	n.t.	n.t.	-416	n.t.	n.t.	-234	-1320
EC	3.5	4.3	n.t.	n.t.	6.0	3.8	2.4	n.t.	n.t.	10.5	5.9	9.2	6.8
T-CR	-	<1E-5	<1E-5	-	-	<1E-5	<1E-5	<1E-5	-	-	-	<1E-5	<1E-5
CU	-	<1E-5	0.080	-	-	<1E-5	<1E-5	0.025	-	-	-	<1E-5	n.t.
BOD	n.t.	0.11	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.
TEN	n.t.	-1.7	-3.5	-1.7	-2.5	n.t.	n.t.	-3.6	-2.2	n.t.	n.t.	n.t.	n.t.
COD	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.
FE	-	5.0	-	-	-	4.4	5.3	8.7	-	-	-	1.7	n.t.
PHE	-	n.t.	-0.32	n.t.	-	-0.06	-0.10	-0.25	-	-	-	-0.10	n.t.
F	2.0	2.5	1.6	n.t.	1.7	2.5	4.1	n.t.	0.6	6.0	4.4	n.t.	n.t.
HG	-	<1E-5	-	-	-	<1E-5	<1E-5	<1E-5	-	-	-	<1E-5	<1E-5
D-HID	-	-0.006	-	-	-	n.t.	-0.004	-	-	-0.019	-	-0.007	-0.003
K	n.t.	-0.03	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.
TSS	0.17	0.11	0.24	0.90	0.50	1.00	0.52	1.04	n.t.	0.13	n.t.	-0.20	n.t.
MG	-0.23	n.t.	-0.10	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.
MN	2.5	0.7	-	-	-	1.7	1.5	2.4	-	-	-	0.5	n.t.
NA	n.t.	0.27	n.t.	n.t.	n.t.	0.21	-0.43	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.
NH4	-	n.t.	-0.008	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	-0.005	-0.007	-0.004	n.t.
NO3	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.	n.t.
DO	n.t.	-0.050	0.078	n.t.	0.051	0.020	0.050	0.141	0.100	n.t.	0.073	0.038	n.t.
PB	-	<1E-5	-	-	-	<1E-5	<1E-5	<1E-5	-	-	-	<1E-5	<1E-5
pH	0.015	0.017	0.019	0.020	0.017	0.017	0.014	0.021	0.023	0.022	0.022	0.021	0.019
PO4	-0.005	-0.008	n.t.	-0.025	-0.031	-0.029	-0.028	-0.047	-0.050	-0.010	-0.019	-0.024	-0.026
SO4	n.t.	0.72	n.t.	n.t.	n.t.	1.08	-0.44	n.t.	n.t.	n.t.	n.t.	1.40	n.t.
W-TEMP	0.060	0.057	0.050	n.t.	0.042	0.103	0.181	0.089	0.156	n.t.	0.030	0.078	0.063
A-TEMP	n.t.	-0.100	-0.057	n.t.	0.089	n.t.	0.272	n.t.	0.167	0.200	0.180	0.101	n.t.
ZINC	-	1.8	-	-	-	1.5	1.9	n.t.	-	-	-	1.0	1.7
WQI	-0.44	-0.44	n.t.	n.t.	-0.50	-0.24	-0.28	0.37	-0.29	-0.45	-0.20	n.t.	-0.55

Of the studied trends, 48 % of the cases were not detected. A positive trend was detected in 37 % of the stations, and negative in 15 %. Amongst the parameters that present a major number of detected trends, the pH stands out. A concentration increase was

detected on many of the studied stations: Cyanides (85 % of the stations), the temperature of the water (85 %), electrical conductivity (69 %), fine (69 %), solid in suspension (69 %), dissolved oxygen (62 %), total chromium (54 %) and arsenic (54 %). As for detected negative trends, the most significant are phosphates (92% of the stations) and the WQI (69 %). For parameters such as Ca wealth, Cl, BOD, COD, K, Mg, NO3, a trend was detected on less than 80 % of the stations.

Phosphate is the parameter that shows the greatest degree of variation throughout the studied period. The variations were superior to 3 % per year in all the cases, especially in station 9, where there was an annual decrease of 11.6 %. Figure 5 (Yearly temporal variation of phosphate (1981-2004)) details the annual evolution of this parameter for each of the stations. A decrease in concentration can be clearly observed over time in all points. The reason for the reduction in concentration of phosphates in the whole basin could be due to the reduction of the quantity of phosphate base fertilizers in the agriculture. This is mainly caused by modernisation in agriculture techniques by means of drip irrigation system.

The light increase of the pH (0.5 % per year) in the whole basin must also be highlighted. This is a very small variation in relation with the totality of the studied stations. The reason for this variation has not been determined.

WQI decreased in nine sites, increased in Site-8 and showed no trend in Site-3, Site-4 and Site-12 (Fig. 6) during the study period (1981-2004). This means a decline of the general water quality. However, in the last five years there has been an increase in WQI parameter, which means a general improvement of the water quality.

4. Conclusions

River water quality networks generate multidimensional data that needs to be statistically studied to analyse and interpret the underlying information. PCA has found a reduced number of 'latent' variables (principal components) that explain most of the variance of the experimental data set. A varimax rotation of these PCs led to a reduced number of PCs, each of them related to a small group of experimental variables with a

hydrochemical meaning: natural factor PC1 (geogenic), PC2 (turbidity), PC3 (climatic) and anthropogenic factor PC4.

Cluster analysis has found spatial similarities in station variations across the river, reducing the number of sites to three (one per group). The first group (sites 1-5) is located at the top of the river (clean waters). In the middle of the river we get the second group (sites 6-8, highly contaminated) and the last group is located at the end of the river, similar to the first group (sites 9-13). Highly polluted waters located in the middle river are surrounded by higher population density across the basin.

Trend analysis with the Mann-Kendall Test and Sen's slope estimator, demonstrated higher reduction in phosphate concentration across the whole river (reduction >3% per year in all cases), due to a reduction of the quantity of this kind of fertilizers.

WQI decreased in nine sampling sites during the study period (Site-1, Site-2, Site-5, Site.6, Site-7, Site-9, Site-10, Site-11 and Site-13) (Figure 6. Yearly temporal variation of WQI (1981-2004)). It shows no trend in three sites (Site-3, Site-4 and Site-12) and an upward trend in one (Site-8).

The combination of WQI and trend detection gives a unique insight into general water quality evolution of each sampling site with time so that it is easily understood by the general public.

Acknowledgements

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