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A chemometric approach to the evaluation of atmospheric and fluvial pollutant inputs in aquatic systems: The Guadalquivir River estuary as a case study

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By combining trace environmental analysis and selected chemometric tools atmospheric and fluvial inputs of pollutants in rivers may be identified. The extension of the pollution originated by each anthropic activity developed along the River may be established, as well as the identification of the pollution introduced into the river by the tributary rivers (point sources) and by rains (non-point sources).

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ABSTRACT

To establish the quality of waters it is necessary to identify both point and non-point pollution sources. In this work, we propose the combination of clean analytical methodologies and chemometric tools to study discrete and diffuse pollution caused in a river by tributaries and precipitations, respectively.

During a two-year period, water samples were taken in the Guadalquivir river (selected as a case study) and its main tributaries before and after precipitations. Samples were characterized by analysing nutrients, pH, dissolved oxygen, total and volatile suspended solids, carbon species, and heavy metals. Results were used to estimate fluvial and atmospheric inputs and as tracers for anthropic activities.

Multivariate analysis was used to estimate the background pollution, and to identify pollution inputs. Principal Component Analysis and Cluster Analysis were used as data exploratory tools, while box-whiskers plots and Linear Discriminant Analysis were used to analyse and distinguish the different types of water samples.

1. Introduction

Classification of fresh waters can be based on quality requirements for a specific use, for example drinking or domestic, public, industrial, agricultural, or recreational use, and so on (EU Directive, 2000). The main difference between these types of waters is the amounts of impurities they contain, which come mostly from human activities. Water pollution sources may be classified as point and non-point sources, which may include atmospheric waste loads that may scavenge by precipitation (Packett et al., 2009; Rouvalis et al., 2009). Point sources are often related to discrete anthropogenic pollution inputs such as sewage or industrial effluents (Buzier et al., 2006; Sañudo-Wilhelmy and Flegal, 1992). Tributary rivers can also be included as point inputs (Berzas-Nevado et al., 2009), and they may present an important influence on the rivers into which they flow, especially when they carry urban sewage, industrial wastes, or mining residues (Vicente-Martorell et al., 2008). On the other hand, non-point inputs are usually associated with agricultural runoff, which enters a water body in a diffuse way (Komaćrek et al., 2008; N'guessan et al., 2009; Franco-Uría et al., 2009), or with rains, which can affect water courses by direct precipitation (Kayhanian et al., 2008) or by runoff (Zhu et al., 2009).

The Guadalquivir River is among the major sources of freshwater in the European Atlantic basin. It is the vital artery of the Andalusian region and, after crossing Córdoba and Seville, it flows into the Atlantic Ocean next to the Doñana National Park. In previous works, we have reported data on the water quality of Guadalquivir River as well as on the evaluation of natural and anthropogenic sources of pollution affecting the river (Mendiguchía et al., 2004, 2007). In this work, chemometrics have been used to analyse new and extended data to study tributaries' pollutant loads as well as atmospheric inputs received by the river after precipitations.

2. Material and methods

2.1. Study site

We studied the navigable part of the Guadalquivir River (SW Spain), with a length of about 115 km, from Alcalá del Río, where a dam controls the flow of the river, to the mouth. About 20 km downstream of the starting point of the study, the river passes through the town of Seville, which has a population of more than 700,000 inhabitants. It is the main urban and industrial centre of an urban agglomeration of about 1,400,000 inhabitants. Its industrial and domestic wastewaters are treated before being discharged into the river. The five wastewater

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treatment plants (WWTPs) with secondary depuration systems discharge over 250,000 $m^3\ d^{-1}$ of treated effluents into the river. Three of these WWTPs discharge into the main course of the river, while the other two discharge into a tributary, the Guadaira River (RG).

In addition to the Guadaira River, two tributary rivers were located in the study zone: the Ribera de Huelva River (RH) in the northern part and the Guadiamar River (BT) close to the mouth. Also, in the middle part, the river has a dock (D) for ships to deliver cargoes to the Port of Seville and to gain access to the shipyards.

As a consequence of the activities developed in the area, the river water may present higher levels of several variables. It is what we call "background pollution", which may affect to water quality.

2.2. Sampling procedures

To characterize the background pollution and water quality of the river, up to 14 sampling stations (G1–G14) were selected along the river (Fig. 1). Also, four additional sampling sites were located at the entrance of the three tributary rivers and the dock. Thus, 72 samples were taken in the four sampling campaigns conducted during a two-year period after the wet season (February 2007 and April 2008) and the dry one (October 2007 and November 2008).

To characterize the effect of rains on the river, five representative stations were selected (G1, G5, G6, G10, and G11) and up to 22 samples were taken within 24 h of each precipitation event.

Different samples were collected for physico-chemical variables, inorganic nutrients, carbon species and total nitrogen, and heavy metals. To provide reliable and accurate data, especially for ultratrace heavy metals, clean techniques were used for handling and analysing samples, as described elsewhere (Mendiguchía et al., 2007).

2.3. Analytical procedures

Conductivity/salinity, pH, and dissolved oxygen (DO) were measured on-board by an electrochemical portable device (Sension 156, Hach Co., USA). Total (TSS) and volatile suspended solids (VSS) and nutrients were determined by gravimetry and standard spectrophotometric methods, respectively (Martín-Galvín, 1995; Rodier, 1990; Tovar et al., 2002). Total dissolved nitrogen and carbon species were determined by a multi N/C 3100 carbon and nitrogen analyser (Analytik Jena, Germany).

For Co, Cd, Ag, Pb, Ni, and Zn, samples were pre-concentrated in a 10,000-class Clean Room by solvent extraction with 1-pyrrolidine-dithiocarbamate/diethylammonium-diethyldithiocarbamate (Bruland and Frank, 1983) and then quantified on a Series X7 ICP-MS (Thermo Electron, USA), employing ^{89}Y, ^{103}Rh, and ^{209}Bi as internal standards. Mn and Cu were determined directly by an AAnalyst 800 GF-AAS (Perkin–Elmer, USA) (Cabon, 2002).

2.4. Statistical procedures

Box and whiskers plots were used to represent the profiles of the variables along the river, and to estimate the importance of tributary rivers and rain events as pollution sources. Trend lines for background pollution were constructed using average concentrations, and an interval of $\pm 0.74 \times s$ was used as the normal expected values.

Normality and homogeneity were tested by the Kolmogorov–Smirnov and Levene tests respectively. Then, two-way ANOVA or Kruskal–Wallis tests were used to establish the existence of spatial and seasonal (temporal) variations in the variables measured in the river (Miller and Miller, 2005).

Principal Components Analysis (PCA) and hierarchical Cluster Analysis (CA) were applied to standardized data (z-score scaling) to elucidate any relationship between sampling sites and/or variables and to classify the different zones of the river according to water quality. Principal components with eigenvalues higher than 1 were retained, and varimax rotation was used to clarify the pattern of loadings. For CA, Ward's method was applied and the results obtained were represented in a dendrogram (Miller and Miller, 2005; Ortiz and Sarabia, 2007).

Finally, using Linear Discriminant Analysis (LDA), a predictive model for tributary rivers and rain events classification was constructed (Ramis and García, 2001). Discriminant functions were constructed to discern the chemical properties of different zones of the river (urban, agricultural, and estuarine) and then applied to predictive classification of cases. Normality and tolerance tests were previously carried out, and all the variables were used for LDA except dissolved organic carbon (DOC) and VSS.

Chemometric data analysis was performed with SPSS Statistics 17.0.

3. Results and discussion

3.1. Background pollution

According to the results obtained by ANOVA or Kruskal–Wallis tests, no significant temporal variations were observed in the chemical characteristics of the river water. However, some specific differences between sampling campaigns were observed and will

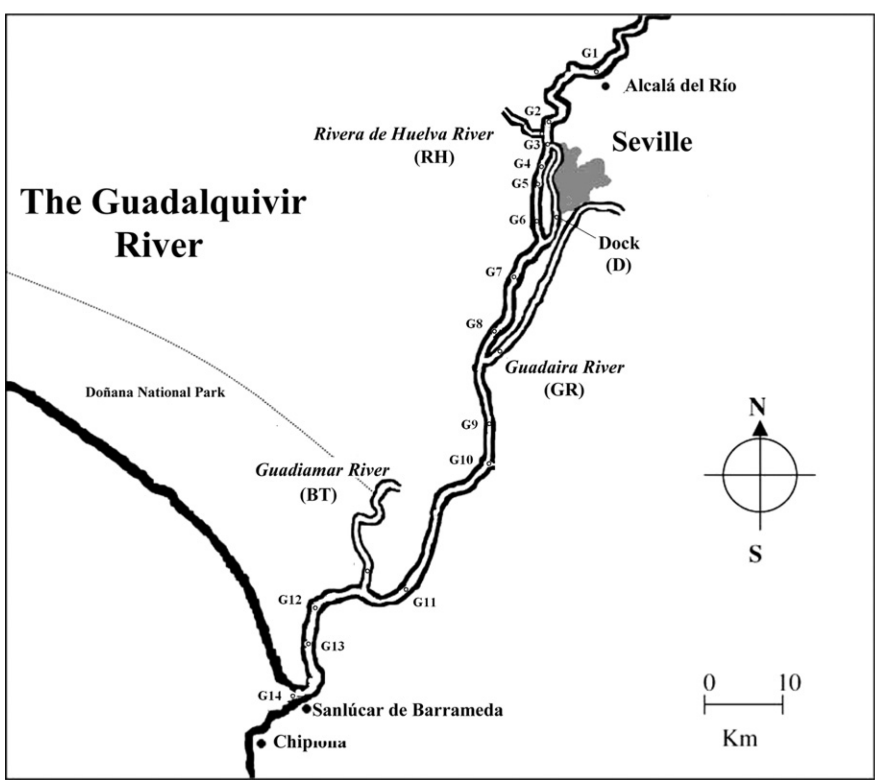

Fig. 1. Map of the Study Site.