Physico-chemical characteristics of the Agüera River (Spain) during an unusual hydrologically period

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Keywords : River, Basque Country, drought, physico-chemical characteristics.

Spatial-temporal changes in the physico-chemical characteristics of the Agura river (Basque Country and Cantabrian region, Spain) were studied over six months, a period that included a long period of unusual drought and the return to more normal hydrological conditions. The chemical composition of the water was affected by water flow. It was influenced either directly through the drainage characteristics at the level of different parts of the surrounding basin, or indirectly through the action of biotic communities on their environment. From these results, some spatial and/or temporal models have been developed for the dynamics of the different variables in this study.

Caractéristiques physico-chimiques de la rivière Agüera (Espagne) au cours d'une période hydrologique inhabituelle

Mots clés : Rivière, Pays-Basque, sécheresse, caractères physico-chimiques.

Les changements spatio-temporels des caractéristiques physico-chimiques de la rivière Agüera (Pays-Basque et Région Cantabrique, Espagne) ont été étudiés pendant 6 mois, englobant une partie d'une longue période de sécheresse inhabituelle, et le retour à des conditions hydrologiques plus normales. La composition chimique de l'eau était contrôlée par le débit de la rivière. Elle est influencée soit directement par l'écoulement au niveau de différents compartiments du bassin versant soit indirectement par l'action des communautés biotiques sur leur environnement. De ces résultats, des modèles spatio et/ou temporels ont été décrits pour la dynamique des différentes variables étudiées.

1. Introduction

Rivers are systems that transport and process materials exported by terrestrial ecosystems, normally seawards. In this sense, they can provide integrated information about the whole of the biotic and abiotic processes occurring in the fluvial basin (Rochelle et al. 1989, Sabater et al. 1990). The relative importance of these functions depends upon a broad series of factors among which physiographic, climatic and biological factors can be cited (Schumm 1988). Man is today a powerful modulator of the environment, and accordingly, his activity may have great influence on the characteristics of river systems (Davis 1987, Reynolds et al. 1989).

Among all the factors cited above, climate, as a regulator of the water flow, exerts an important control over the fluvial communities (Scrimgeour & Winterbourn 1989) ; very often they have to face relatively unpredictable changes in their environment, which can affect their biomass, the structure and composition of sediments, the physico-chemical composition of water, etc. (Reiter 1986). Therefore, it is always interesting to study the response patterns of different reaches of a river to changes in their hydrological regime.

Northern Iberian rivers flowing to the Cantabric sea are characterised by their heavy slope and short length, and, in contrast to those flowing to the Mediterranean, do not show important temporal variations in their discharge rates. Up to date, the studies carried out in different catchments of the Basque Country (Euskoiker 1988) have contributed only with low-periodicity data of several

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physico-chemical variables, but they have not allowed a detailed analysis of short-term changes in the rivers. In this paper, we present the results of a study of the physico-chemical properties of the river Agüera, carried out during the final phase of a long and unusual dry period and the beginning of more usual hydrological conditions.

2. Study site

The Agüera river (Basque Country-Cantabria, Spain) drains a basin of 14,500 Ha (Fig. 1), whose highest point is mount Burgueño (1 044 m a.s.l.). The river runs 30 km until it reaches the sea. From the geological point of view, the basin lies over a Cretaceous, mostly siliceous substrate, covered with sandstones and clay, except in a broad central strip, where marls and very thick, karstified limestones predominate. Several springs can be found in this zone, which indicate the importance of the aquifers (Cruz San Julián et al., 1986). Main land uses are grasslands and agricultural lands (29 %), forestal plantations (mostly pine, 34 %, and Eucalyptus, 16 %), and autochthonous forests, mostly oak (10 %) in siliceous land, cantabric evergreen oak (7 %) in calcareous substrate, and alder in the margins of the river channels. Population density is low, and the principal

human activities are agriculture, livestock, and forestal sectors. Human settlements are disperse, and the biggest villages are those of Trucios, Villaverde, Guriezo and Trebuesto. The climate is humid-oceanic, with an annual precipitation of 1,650 mm, almost totally in form of rain, regularly distributed throughout the year. The annual mean temperature is 11 °C, and the monthly mean varies between 5.8°C in January and 17°C in August.

During 1988-1989 an unusual drought was registered, as the habitual fall-winter rains failed. The waterflow maintained low levels, reaching its minimal values in January-February (Fig. 2). This dry period ceased suddenly at the end of February, and the waterflow was high during March. April was a very rainy month, reaching the highest discharge of the last five years on 4th April.

3. Methodology

Ten stations located along the whole river (Table 1), were sampled biweekly during six months (November 88-May 89). The following variables were determined *in situ*: cross section of the channel, velocity distribution of the water (flowmeter General Oceanic), pH (pHmeter Scharlau Hi 8424), temperature, conductivity (conductivimeter WTW

Table 1. Main characteristics of the sampling stations.

Station	Km	Elevation (m)	Slope	Order	Vegetation
1	1	450	19.05	1	Mixed forest
2	3.3	230	3.08	2	Pines
3	4	210	1.7	3	Meadows
4	7.3	150	0.71	3	Meadows
5	10.5	130	0.69	3	Meadows
6	12	120	0.86	3	Meadows
7	15.5	80	0.8	3	Eucalyptus
8	18.5	60	1.33	3	Meadows
9	24	15	0.44	3	Meadows
10	25.3	5	0.44	3	Meadows

Fig. 1. The Agüera river basin. Main geological features and human settlements are showed. Numbers correspond to the sampling sites.

Fig. 2. Discharge variations in Agüera river from 1984 to 1989. Compare the study period with the values in the upper part of the figure.

LF90), concentration and percentage of saturation of oxygen (oxymeter WTW Oxi96). Water samples were taken in plastic bottles, and immediately introduced in a cool place to be carried to the laboratory. Samples for the determination of phosphate were also preserved in cool conditions, but in glass bottles.

The following variables were determined according to the Standard Methods (APHA 1980): alkalinity and hardness, by titration; magnesium, sodium and potassium by atomic absorption spectrophotometry; calcium by calculation from the difference obtained in the analysis of hardness and magnesium; soluble reactive silicate, nitrate, nitrite,

ammonia and reactive phosphorus by spectrophotometry; sulphate by the turbidimetric method; fine sestion (< 1 mm), after filtration (Whatman GF/C), oven drying (70°C) and calcination (450°C). Measurements of alkalinity and hardness were conducted immediately and the remaining samples were maintained at 4° C until their processing. Whenever the analysis was impossible to be made within the first 24 hours, the samples were kept frozen at -20°C.

4. Results

A clear longitudinal gradient can be seen in the variables associated with the mineralization of waters, conductivity, hardness, and alkalinity (Fig. 3a, b, c). They show notable increases around station 4, where the river passes from the siliceous to the calcareous part of the basin. The pH (Fig. 3 d) shows a similar pattern, but it diminishes in the final reaches of the river, as a consequence of the contribution of low-mineralization affluents.

Fig. 3. Spatio-temporal variations during the study period. a) conductivity ($\mu\text{S}/\text{cm}$); b) hardness (meq/l); c) alkalinity (meq/l); d) pH.

This condition becomes more and more evident as the flow decreases in winter, and suffers a drastic change with the floods in February-April, with the result of a remarkable homogenization of the river at high flows.

The oxygen saturation (Fig. 4 a) also shows important temporal variations. On the one hand, strong oversaturation levels are found in station 1. We associate this phenomenon with waterfalls just above the measuring site. On the other hand, at the end of the dry period, very high partial tensions of

oxygen are detected in the intermediate and final stations, probably caused by the metabolism of benthic communities. The saturation of oxygen is almost reached at stations 7 and 8, partly due to the steeper sides, and to the SE-NW direction of the streambed, which determines low incident irradiances during the winter months, and partly to their greater turbulence, involving a faster gaseous interchange with atmosphere. In high-flow periods, the oxygen concentration is around saturation throughout the river.

Fig. 4. Spatio-temporal variations during the study period. a) percentage of oxygen saturation; b) nitrate concentration ($\mu\text{gN/l}$); c) nitrite concentration ($\mu\text{gN/l}$); d) ammonia concentration ($\mu\text{N/l}$).

Fig. 5. Spatio-temporal variations during the study period. a) phosphate concentration ($\mu\text{gP/l}$); b) silicate concentration (mgSi/l); c) suspended fine particulate matter (mg/l); d) percentage of organic content of FPM.

Nitrate (Fig. 4 b) seems to reflect two overlapped phenomena. Its levels are highest in the period November-January, decreasing from there on; this seems to reflect a seasonal rhythm. On the other hand, its concentration increases with high discharges, mostly in headwaters. Nitrite (Fig. 4 c) usually appears in low concentration, reaching its highest values downstream from the human settlements, i.e., stations 4, 5, 9 and 10. Furthermore, a temporal variation is observed, as the content of this

nutrient decreases during January-February, and increases again when the discharge rises. Ammonia (Fig. 4 d) shows a less regular pattern, possibly due to the very local factors that govern its concentration.

Phosphate (Fig. 5 a) also reflects the importance of the wastewaters associated with the villages of Villaverde, Trucios and Guriezo, and the subsequent recovery process. Silicate (Fig. 5 b), reaches its

Fig. 6. Situation of the measured variables in the plane of axis I and II resulting from PCA. TE : temperature ; pH : pH ; CON : conductivity ; SAT : oxygen saturation ; OX : oxygen concentration ; FLO : waterflow ; ALK : alkalinity ; HAR : hardness ; Ca : calcium ; Na : sodium ; K : potassium ; Mg : magnesium ; SIL : silicate ; NAT : nitrate ; NIT : nitrite ; AMO : ammonia ; PHO : phosphate ; SU : sulphate ; SES : seston ; FOM : fine particulate organic matter.

variable, although always high. On the other hand, stations 7 and 8 show, except for spates, a trend to be situated in a narrow band in the positive part of axis II. This phenomenon is in agreement with the self-depuration occurring in this reach.

5. Discussion

Differences in the lithological composition of the Agüera river basin are responsible for a pronounced longitudinal gradient in the parameters associated with water mineralization, mostly in dry periods, when the contact between the water and mineral substrate is most intense. In any case, there are

values of pH that are explainable not only by the kind of substrate, but also by metabolic processes of the community. This is especially evident during February, a period of minimal flows, that, possibly in combination with the elongation of the day, make easier the proliferation of benthic algae in medium reaches. In this part of the river, important algal masses, dominated by *Cladophora* sp., can be observed. The metabolism of these producers could be the responsible for high pH values (Margalef 1983), as those found in stations 4-7. This is also deduced from the diel dynamics of this parameter (unpubl. data). In lower reaches (station 9) this effect is not so evident, possibly because it is counteracted by the decomposition of organic materials of urban origin.

Fig. 7. Situation of the samples in the plane of axis I and II resulting from PCA.

The results of this work have allowed us to deduce spatial and/or temporal patterns in the dynamics of the different non-conservative variables studied. Nitrogen, under its different forms, constitutes one of the essential nutrients in rivers. Biological transformations of nitrogen include the uptake by algae and microbes, fixation and denitrification (Richey et al. 1985, Hill 1988), but estimates of the relative importance of these processes in different rivers do not coincide. In our case, nitrate concentration increased with high discharges, mostly in the headwaters, probably due to the greater leakage of soils (Mc Diffet et al. 1989). Several authors (e.g. Neill 1989) stress the importance of the agricultural practices, like the fertilization of ploughed land, in the control of nitrate levels in rivers. From our results

it can not be deduced any clear relationship between agricultural land and nitrate concentration. This is explainable by the kind of agricultural practices in this area, in which meadows are the most important crop, with not very intensive application of mineral fertilizers. Nitrite maxima appear near the main urban settlements. Also, as the importance of producers increases in February, maximum values of nitrite decrease, possibly helped by the oxidizing conditions that prevail at that moment. When rainfall increases, nitrite maxima appear near the villages, as a consequence of the leaching of rivershore areas. The dynamics of ammonia are more complex, and in this sense, we cannot forget the several sources of ammoniacal nitrogen (Schuurkes & Mosello 1988), which obscures their interpretation.

Phosphate clearly reflects the influence of the villages, but with this sampling strategy we cannot ascertain its importance in relation with other possible factors of variation, as the agricultural practices in karstic areas (Troelstrup & Perry 1989), the urbanizations (Osborne & Wiley 1988) or the biological uptake (Corning et al. 1989, Mulholland et al. 1983). In the Agüera river, self-purification processes (Vymazal 1988) are evident in the reach where urban inputs disappear, that is, in the reach 6-8, during low-flow periods. According to Corning et al. (1989), the assimilation rate of phosphate by the benthos does not change along the river. If that is the case of our system, we should explain the decrease in medium-low reaches as a mere reflection of the disappearance of phosphorus inputs; the high capacity of self-purification in the river would be exceeded solely by important inputs around villages. On the other hand, Cosser (1989) mentions the importance of particulate phosphorus. A part of the decrease in the charge of phosphorus could be due to the sedimentation of seston, which would be favoured in the reach 6-8, that seems to be especially retentive.

During February, the high organic content of the seston in medium-low reaches in coincidence with the vicinity of villages, seems to be due to the low flows of this dry period, that would concentrate the sewage. The drift of algae in medium reaches could be added to this effect, as these organisms were particularly abundant during this period. We can deduce that river discharge is the principal responsible for the FPOM concentrations, in agreement with other works (Cuffney & Wallace 1989, Grubaugh & Anderson 1989). These authors report that most of the yearly transport of the organic matter occurs in a few events.

The Principal Components Analysis stresses the spatial organization of the Agüera river. It could be divided in four main zones. In the headwaters, up to station 3, most of the catchment area is forested, the slope is high, and human activities minimal; these properties determine, together with the lithological composition of substrate, low nutrient concentrations in the water, and a scarce importance of primary producers. A second zone would correspond to the reach between stations 4 and 6. Here, both the population density and the intensity of agricultural practices rise. All this, together with the smaller slope and the lower forest cover, makes

possible, under medium and low flow conditions, the blooming of dense algal populations, even in winter months. In this sense, Sheldon & Taylor (1982) showed, in artificial rivers, the relative constance of algal production during the year, in contrast with the more seasonal effect of macrophytes. In the third zone, situated between stations 6 and 8, the physiographic characteristics of the reach determine a process of self-purification. In fact, in this part, human activities diminish, the slope rises, streambeds are steeper, and the streambed consists of a series of riffles and pools, that makes this a highly retentive reach (Cummins et al. 1983, Webster et al. 1987). The last part of the river, located between station 8 and the mouth, is again more open, more humanized, and as a consequence, nutrient levels increase. This spatial organization is changed by the discharge, with floods producing an homogenization of the chemical characteristics along the longitudinal axis of the river, as a consequence of the diluting effect of the water, and the disturbance of benthic communities.

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