A simple multi-criteria approach to delimitate nitrate attenuation zones in alluvial floodplains. Four cases in south-western Europe

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Highlights

- A comparative study of four riparian zones of Southwest of Europe is conducted
- The approach is based on a one year monitoring: hydrochemistry and flow net
- River-floodplain-upland connectivity and C and N source-pathways are considered

- Indicators to map the attenuation zones are proposed

Abstract

Four alluvial floodplains were selected in the European southwestern lowland area: the rivers Ebro, Bidasoa, Tagus (Spain) and the Garonne (France) were chosen. They have some common characteristics (alluvial aquifers, connectivity with the river, nitrate pollution) but differ in other important aspects (water table fluctuations, flooding dynamics, landscape control, land use, agricultural practices, climate). A comparative study considering nitrogen and carbon sources and the way they interact in the riparian zone was conducted in order to test a simple approach to delimitate permanent nitrate attenuation zones and to evidence the importance of site-specific attributes. The observation was based on a detailed monthly monitoring during a year ensuring data at high and low water periods. The tested approach results in a useful tool to spatially delimitate the attenuation zones. However, this approach is difficult to apply in areas where pollution sources are very diverse in type and in both time and space. This leads us to conclude that a general conceptual model cannot capture all the factors needed to understand the nitrate removal dynamics of a riparian zone. Hence, the study combines observation-conceptualization framework with river-riparian-upland connectivity and source-pathway-target continuity.

Keywords: Riparian areas, detailed monitoring, connectivity, flooding, attenuation zones mapping, nitrogen and carbon sources.

1. Introduction

Aquifers and rivers have traditionally been considered as independent compartments in the environment (Smith et al, 2009). Recent legislation, as the EU Water Framework Directive (WFD, 2000), emphasizes the need for an integrated management of river catchments, including better understanding of water exchange between aquifers (GW) and rivers (SW). These exchanges are usual in riparian zones where GW-SW interface may extend several hundreds of meters from the river, depending on the site-specific conditions. The surface-groundwater interface supports the purification of water by attenuating nitrates in the vegetation-soil system and in the aquifer (Sánchez-Pérez et al., 1991a, 1991b; Takatert et al., 1999). The riparian landscape is unique among environments because it is a terrestrial habitat strongly affecting and affected by aquatic environments (Mander et al., 2005). Its role has been highlighted as ecotone or as corridor, but in both the cases the riparian zones can act as conduits, filters or barriers controlling flows of energy, matter and species in landscapes (Burt et al., 2013). Some authors refer to them as Hyporheic Zone (Booker et al., 2008; Marmonier et al., 2012).

Often the riparian zone is taken to be synonym for floodplain, formed mainly of river sediments and often influenced by overbank flooding events, so that it connects upland and river through surface and subsurface hydrologic flow paths (Naiman et al., 2005; Burt et al., 2013).

Intersecting these flow paths produces dynamic moisture and biogeochemical conditions in which processes impacting on the fate and transport of solutes can occur (Korom, 1992; Cirmo and McDonell, 1997; Gold et al., 2001; Vidon and Hill, 2004). As the moisture and biogeochemical conditions are heterogeneous in both space and time “hot spots” and “hot moments” concepts have been developed (McClain et al., 2003) to describe the function of riparian areas as buffer zones. The “hot” terms refer to a disproportionately high reaction rates relative to the surrounding area (spot) or to longer time periods (moment). Though the authors focused on N and C these concepts may also apply for a wide variety of constituents (Vidon et al., 2010).

Vidon et al (2010) add a new step by distinguishing between transport-driven and biogeochemical process-driven hot spots and moments, which aims to highlight if the cause being behind the high reaction rate is a biogeochemical process or a transport event, although these phenomena should be considered simultaneously. As regarding denitrification, biogeochemically active hot spots in aquifers of the riparian zones are formed where flow paths with high concentrations of electron acceptor species (mainly oxygen, nitrate) intersect flows, or patches, with high concentration of organic carbon. Sources (point or non-point) and pathways (surface water or groundwater) of these elements are site-specific, and therefore vary from one riparian zone to another. The hydrological conditions at the river-groundwater interfaces have been shown to have a significant impact on denitrifying processes in aquifers (Lamontagne et al., 2005; Rassam et al., 2008). In riparian zones where groundwater levels are lower than soil root zones, denitrification has been found to attenuate nitrate efficiently in groundwater. In these conditions, the recharged river water, rich in organic matter, has stimulated the occurrence of denitrification (Sánchez-Pérez et al., 2003b; Iribar et al., 2008, 2015).

Agricultural activities are known to be a significant source of nitrate in groundwater. As alluvial plains, and mainly plateau areas feeding them, support intensive agricultural activities, they often suffer from groundwater nitrate pollution (Sánchez-Pérez et al., 2003a; Almasri and Kaluarachchi, 2007). As this pollution has become a significant environmental problem the ability of riparian buffers to remove agricultural contaminants has been studied extensively (McCarty et al., 2007; Rivett et al, 2008; Williams et al., 2014) and biological denitrification has been identified as a primary pathway for nitrate removal. Microbial "hot spots", with significant denitrification activity, have been found in patches of organic-rich soil and also at depths of several meters in zones near interfaces of different types of flows (McCarty et al., 2007). Among several factors controlling biological denitrification, hydrology and hydrogeology (Maître et al., 2003; Vidon and Hill, 2004; Lewandowski et al., 2009; Landon et al., 2011; Williams et al., 2014), geomorphology (Gold et al., 2001), geology and land use (Dosskey et al., 2010; Español et al., this issue), all of them as a continuum, can influence nitrate removal capacity of the riparian zones. Classifications based on these attributes have been proposed in order to fulfill requirements of the Water Framework Directive (Dahl et al., 2007).

The hillslope-riparian-river connectivity (McGlynn and McDonnell, 2003; Klaus et al., 2015) is widely acknowledged as a fundamental property of all ecosystems and has been taken as a primary element in conceptual model describing dynamics in riparian areas (Peyrard et al., 2008; Opperman et al., 2010). Lowrance et al (1997) pointed out some of the most important multifunctional elements that riparian biotopes present (filtering pollutants, protecting riverbanks, regulating flows, improving microclimate, creating connectivity). Other authors (Opperman et al., 2010; Burt et al., 2013) emphasize floodplains as geomorphic features upon which ecosystems with immense ecological and economic value develop. According to this, efforts must be made to identify and manage hot spots for a better attenuation of pollutants by acting on disturbed riparian zones. In this way restoring hydrologic connectivity (Kondolf et al., 2006) or recovering forest areas to enhance biogeochemical processes (Burt et al., 2013; Comin et al., this issue) have been proposed. Booker et al. (2008) establish a typology of Hyporheic Zones based on their pollutant attenuation capacity and prioritize field data in order to determine the distribution and variability of environmental variables.

In this paper we are interested in the identification of hot spots in riparian zones. In fact, as pointed out by Vidon et al (2010) "developing monitoring techniques to map the distribution of biogeochemical hot spots in riparian areas is likely to remain a particular concern in the future because other relevant fine-scale data that reflect physical and biological soil heterogeneity are not yet readily available". Our study has been carried out in the framework of the Attenagua Project. It is a research project INTERREG IVB SUDOE (Southwest Europe) funded by the European Regional Development Fund (ERDF). The main objective is to develop a method to identify the best locations for the use of the riparian area groundwater to supply drinking water. This involves taking advantage of self-purification capacity in riparian floodplains, namely denitrification. The method is based on the integration of the knowledge on physical-biogeochemical interactions in four alluvial riparian areas (lowland of the rivers Ebro, Bidasoa, Garonne and Tagus). These sites were chosen because of their differences in hydrology, landscape, land cover and anthropogenic context representative of the SUDOE region.

In the Attenagua Project nitrate attenuation activity in riparian areas was characterized by using different methodological approaches based on water physicochemical characterization (Ochoa-Salazar et al., this issue; Bernard-Jannin et al., this issue), characterization of the invertebrate diversity and functionality (Español et al., this issue; Comin et al., this issue; Yao et al., this issue), characterization of the microalgae, analysis of denitrification potential, analysis of the bacterial community structure (Bodoque et al., this issue) and hydrobiochemical modeling (Sun et al., 2015). The present paper deals with the first approach mentioned, so that we take advantage of a high resolution dataset of physicochemical parameters to understand nitrates dynamics in relationship with water fluxes and carbon organic availability.

Based on the results obtained in the study sites, indicators are proposed to map the areas of natural attenuation, depending on the hydrogeological and landscape characteristics and sources of contamination. This paper does not aim to provide accurate spatial representations of the attenuation processes but to provide a good estimation of the attenuation zones (hot spots) with a simple method based on relative few field indicators. Furthermore this knowledge is essential to focus on the issues to be investigated in detail in site-specific research. Specific objectives are: i) To test a simple approach to delimitate permanent attenuation zones in riparian areas as regards nitrate pollution. ii) To put in evidence the importance that site-specific attributes have on these spots. This study combines observation-conceptualization framework with river-riparian-upland connectivity and source-pathway-target continuity.

2. Materials and methods

2.1. Study sites description

Four river meanders (figure 1) located in South-western Europe were selected: the rivers Ebro, Bidasoa, Garonne and Tagus. All of them are characterized by a combination of agricultural occupation and patches of natural riparian forest that might favour the potential degradation of agricultural pollutants. In order to favour the comparison of the study sites (figures 2 and 3) a wide variation of climatic and environmental conditions (land use, landscape, geology, hydrology and hydrogeology) were considered. For a better consideration of processes occurring in the alluvial aquifer, piezometers were grouped according to the distance to the river (land use was not considered in this classification). Three groups were considered: Near River (NR), Intermediate Zone (IZ) and Distant Zone (DZ, usually in or near the pollution source area). This distribution has been used in many of the analysis incorporated in the present paper.

2.1.1. Ebro site

The site (Soto de Nis, 78 ha) is a meander 12 km downstream of Zaragoza, Spain (UTM 686179, 4607010), which is included in the "Los Galachos" natural reserve. It is mostly subjected to agricultural use, corn and irrigated cereals. It shows an extensive riparian corridor dominated by white poplar (*Populus alba*), black poplar (*Populus nigra*), white willow (*Salix alba*) and salt cedar (*Tamarix* spp.). Near the river (forested zone) slope is around 0.13% and it is smaller in a more distant zone which is located in a terrace 3 m above the near river zone (figure 2). River incision is the smallest one in this site, about 1.5 m. Mean annual precipitation and temperature is 380 mm and 15°C, respectively.

The aquifer comprises quaternary alluvial deposits consisting of highly permeable big sized gravels. In this area the aquifer is 7 km wide and over 15 m thick; in fact, previous wells drilled in the area did not reach the bedrock, which is thought to be formed by impermeable evaporitic materials (figure 2). No data are available but hydraulic conductivity must be high. The average water table is located at a depth of between 1.4 m (riparian zone) and 4 m in agricultural areas. The Ebro River (around 25.000 km^2 up to this site) shows a very irregular hydrological regime with high peaks in winter and spring and very low discharge in summer (figure 3). No tributary stream is crossing the study site. Until 1980´s the Ebro River in this area could be defined as a meandering channel, but since them it has undergone modifications which in turn have conditioned relationships with the aquifer. In fact, present near river zone was previously the water course. In the framework of our project a network of 12 piezometers was installed up to 9 m depth. Sampling network was completed with 2 points in the river (figure 1).

2.1.2. Garonne site

This site (Monbéqui, 12 km^2) is located in a meander 50 km north of Toulouse in South-West France (UTM 355758, 4861267). The floodplain (figure 1) consists of irrigated agricultural land (distant zone), corn and sunflower, poplar plantations (intermediate zone) and riparian forest (near river zone), dominated by poplar (*Populus* spp.), ash (*Fraxinus* spp.) and oak (*Quercus* spp.). Topography is almost flat in all the floodplain area (4 km width) with slopes around 0.40%, and the river incision is about 7 m (figure 2). Mean annual precipitation and temperature is 710 mm and 13.5°C, respectively.

The aquifer comprises quaternary alluvial deposits consisting of highly permeable sand and gravel, 4 to 7 m thick, with high lateral continuity (Sánchez-Pérez et al., 2003b). Hydraulic conductivity is around 300 m/d in the river near zone decreasing up to 100 m/d in distant zones (Sun et al., 2015). The average groundwater table is located at a depth of between 1 m (riparian zone) and 4 m in agricultural areas and rise rapidly up to soil profile during floods (Weng et al, 2003). The upper layers of the riverbed and the floodplain are silty. The particularity of the Garonne River in this site (around 13.700 km^2 up to here) is that the water courses over an impermeable molassic bedrock (figure 2), with an annual average flow of 200 m^3.s^{-1} which ranges from 10 m^3.s^{-1} in summer to 2900 m^3.s^{-1} in winter and spring (figure 3), (http://www.hydro.eaufrance.fr/). Therefore the exchanges between the river and the aquifer are mainly horizontal and controlled by the river level. The river course has undergone some changes during the last centuries. No tributary stream is crossing the study area. More than 50 piezometers have been installed. However, in order to compare all the study sites with a similar set of points, a network of 13 points (11 piezometers and 2 points in the river, figure 1) was chosen.

2.1.3. Bidasoa site

The site is a meander (Lastaola, 22 ha) located 7 km upstream of Irun, Basque Country, Spain (UTM 602190, 4797250). Agriculture, corn and pasture, and livestock practically cover the entire floodplain, leaving a tight riparian corridor along the river shore (figure 1). Forest area is very small and dominated by white willow (*Salix alba*), alder (*Alnus glutinosa*) and ash

(*Fraxinus excelsior*). Invasive species pokeweed (*Phytolacca Americana*) is abundant. River incision is quite important (5 m) and the slope of the site is quite flat, less than 0.25% (figure 2), being much bigger in the west side where an alluvial fan of a lateral stream is observed. This stream, and the fan, seems to have a high control on the hydraulic response of the aquifer. On this fan there is a farm (dairy), which represents an important point source of pollution. Mean annual precipitation is very high, around 1870 mm, and temperature 13 °C.

Quaternary deposits may be up to 30 m thick but no more than 300 m width (figure 2). This thickness makes the alluvial aquifer interesting, as shown by water extractions in the past during dry periods. The deposits consist of silty sands in the top and highly permeable gravels below. Hydraulic conductivity ranges from 10 to 100 m/d. The silty materials on top make the aquifer to show a semi-confined behavior. Under the aquifer impervious materials, granites and shales, are found. The topography of the bedrock is quite irregular making groundwater upwelling near the river possible. The average water level depth ranges from 4 m, in the distant zone, to 4.5 m. The Bidasoa River (around 700 km^2 up to here) shows a very irregular regime peaking in winter and spring and declining in summer (figure 3). 7 piezometers, up to 9 m depth, were installed. Sampling network was completed with 3 points, 2 in the river and 1 in the lateral stream (figure 1). Wells previously installed were used to complete geological information.

2.1.4. Tagus site

The site (El Soto Redondo, 80 ha) is situated in a meander of the Tagus River, 40 km west of the city of Toledo, Spain (UTM 380482, 4410115). This site is under extensive agriculture, mainly irrigated cereals, vegetables and pasture. Throughout the whole area is applied pig manure to fertilize. Only some isolated patches of riparian forest remain, in a narrow line near the river, being dominated by white poplar (*Populus alba*) and salt cedar (*Tamarix* spp.). River incision is quite important (6 m). Land slope is 0.80% lowland but increases toward upland reaching 1.60% in some terraces (figure 2). Mean annual precipitation and temperature is 375 mm and 15°C, respectively.

The aquifer is composed of unconsolidated deposits, consisting of gravel and clay sediments overlaid by deposits of sand, with a high lateral continuity. Thickness of the aquifer is unknown but it has to be more than 9 m as the piezometers have not reached the bedrock, which consists of impervious granitic rocks. Hydraulic conductivity is around 10 m/d. The water table ranges from 1 m (near river banks) to 5 m inside the meander. The recharge of the aquifer is mainly due to irrigation (Castrejón channel derived from the river is 2 km north), while the hydraulic connection with the river is insignificant because of the Tagus River is highly regulated by dams and water derivations, with a discharge that hardly varied (figure 3) (Bodoque et al., this issue). A network of 10 piezometers, up to 9 m depth, was installed. Sampling network was completed with 2 points in the river (figure 1) and one in the irrigation channel.

2.2. Monitoring system

Observation was based on a detailed monitoring, similar for all the sites. Monitoring network (figure 1) was designed considering the floodplain surface and the land use and consists of 7-12 piezometers. These are 8 to 9 meters long and 60 to 100 mm width; the 1.5 m top of the PVC pipe is blind (the space around was sealed with bentonite) while the rest is screened. In all the sites there are two sampling points in the river (upwards and downwards the meander). In Bidasoa and Tagus another point was included, in the lateral stream in the first site, and in the irrigation channel in the last site.

All of the points were sampled in each site once a month during a year (April/May 2013 – March/April 2014) ensuring sampling at high and low water levels (figures 1 and 3). Four of the twelve campaigns included sediment and biota sampling (Español et al, this issue; Bodoque et al., this issue; Comin et al., this issue; Yao et al., this issue). Groundwater was sampled after pumping, when electrical conductivity (EC) of the extracted water was constant. Samples were kept cold (< 4ºC) in 500 ml plastic bottles and immediately carried to the laboratory for analysis. Dissolved oxygen, temperature, pH, ORP (oxidation / reduction potential) and EC were measured in the field, and mayor anions and cations in laboratory. Data loggers (CTD Divers, Schlumberger Water Services) were installed in some of the piezometers (between 5 and 8 in each site, one of them in the river) to carry out continuous measurements of water level depth, EC and temperature. A Baro-Diver was also installed in each zone for atmospheric pressure control, which is needed to deduce the hydraulic head.

Samples were filtered through 0.45 μm Milipore nitrocellulose filter. One replicate of each sample was acidified to pH<2 with HNO_3 (65%) for base cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and silica analysis, which were measured using ICP-OES (Perkin Elmer Optima 2000). Major anions (Cl^-, NO_3^- and SO_4^{2-}) were measured in the non-acidified replicate using ion chromatography (DIONEX ICS 3000). DOC (dissolved organic carbon) and TOC (total organic carbon) were respectively analyzed in one filtered and one non-filtered replicate using a Total Organic Carbon Analyzer (TOC-L Shimadzu), while POC (particulate organic carbon) was calculated by the difference between TOC and DOC. Alkalinity was determined in the unfiltered sample from the TIC (total inorganic carbon) values measured by the TOC-L Shimadzu. The analysis of the phosphate (PO_4^{3-}) was conducted using the ascorbic acid method (APHA-AWWA-WPCF, 1998) and determined by colorimetric method. Modified Berthelot reaction using salicytate and dichloroisocyanurate was used to determine the ammonium (NH_4^+) by colorimetric method. Analyses were performed on the spectrophotometer Jasco V-630 and all of them showed an Ion Balance Error (IBE) between 10% and -10%.

2.3. Hydrology and Hydrogeology

Discharge of the river is measured in gauging stations located in a relatively small distance (between 3.5 and 20 km) upstream from the sites. There are not significant tributaries in the river between the stations and the studied sites. Discharge is measured every 10 to 30 minutes. However, considering that for our study a coarser time scale is enough, the average daily discharge was used for further analysis (figure 3). In the analysed series discharge necessary to start flooding and to flood around 50% and 100% of the floodplain area was established based on modelling results. MOHID Land (Neves, 1985; Braunschweig et al., 2004) was applied with satisfactory results for simulations of discharge and groundwater level depth (http://attenagua.actionmodulers.dtdns.net/files/ ModellingApproach.pdf). In order to compare the percentage of time that different areas of the four study sites were flooded, flood duration curves were constructed and evaluated taking those data obtained from the model into account. A correlation analysis was applied to daily discharge series from April-May 2013 to March-April 2014, in order to obtain their autocorrelation function. The mathematical development of the method, as applied in hydrology, is well known (Mangin, 1984). This method is used for the comparison of systems with different scales, as the autocorrelation function (r) does not depend on the specific values of the runoff series but rather, on the width and height of the runoff peaks (Grasso and Jeannin, 1994). With regard to groundwater, continuous water level data obtained from the Diver devices were transformed in continuous water depth series. In order to analyze these data in the same time step as discharge, mean daily water depth was calculated for each piezometer. After that, the percentage of time (days) that water level in the aquifer is below a certain depth was calculated (figure 4). Additionally, water table manually measured during each sampling campaign was considered to obtain monthly flow net for each study site. For this purpose, spline analysis of interpolation was performed using ArcGIS 10.1. From those maps two, one for high and another for low groundwater levels, were selected to obtain flow nets for those two situations. Many of the results in the paper are based in those two different hydrological situations.

2.4. Statistical methods

In order to analyze field data variability boxplots were made with some of the parameters measured during the monthly sampling campaigns (water depth, temperature, EC, ORP, O_2, DOC, NO_3^-, Cl^- and NH_4^+ for Bidasoa site only). Boxplots include median, 25th and 75th percentiles, 25th percentile minus and 75th percentile plus (1.5 x interquartile range) and upper and lower detached values.

2.4.1. Principal Component Analysis

Factor analysis is an effective way of interpreting and representing chemical data. The interpretation of factors yields insight into the main processes which govern the distribution of hydrochemical variables. In this work a Principal Component Analysis (PCA) was performed in each study site to give a general description of the site in order to compare them and help identify the connectivity degree between surface water and groundwater as well as water mixing zones and processes. As pointed out by King et al (2014), PCA is one of the most commonly used multivariate statistical analyses of hydrochemical data to assess alluvial aquifer-stream connectivity. This analysis reduces a large number of parameters into fewer components (typically two or three), which can be often used to identify hydrological processes. In addition data are displayed to highlight the hydrochemical evolution of groundwater. In order to make the different groups of waters in each site visible a PCA was performed on a subset of 14 selected variables (EC, Alk, Cl^-, SO_4^{2-}, SiO_2, DOC, ORP, NO_3^-, PO_4^{3-}, NH_4^+, K^+, O_2, Temperature, water depth) which represent the overall geochemical framework of the study areas. Water depth was included as a parameter integrating the connectivity between the river and the aquifer. Factor Analysis (Varimax Rotation) was conducted with the help of SPSS 19 software. The factors considered to be significant were those that showed eigenvalues equal or higher than 1. For discussion we consider parameter loadings classified as strong (values > 0.7) and moderate (0.5 - 0.7).

2.4.2. End-Members Mixing Analysis

With the objective of having more detailed information on the connectivity between river and aquifer an end-member mixing analysis (EMMA) was conducted to estimate the proportion of water from different sources in the mixed water of the aquifer. Basis of the method can be taken from Hooper et al (1990) or Christophersen and Hooper (1992). Ochoa-Salazar et al (this issue) use this methodology to evaluate the usage of metals to characterize hot spots in an alluvial area. Key assumptions for mixing models are: tracers behave conservatively, mixing process is linear, chemical composition of end-members does not change over the time and the space. In the simplest form the contributions of the end-members can be computed by directly solving the mass balance equations for the selected tracers given the observed concentrations of the potential end-members. However, as pointed out by Inamdar (2011) this simple approach does not constitute a true EMMA, which involves the use of a large number of tracers (more than the minimum required to identify potential end-members) within a PCA framework.

We are conscious of what a deep application of EMMA implies. However, we applied this method in a simpler approach according to the objective posed. In fact, uncertainties derive from the high temporal variability of the chemical composition of waters we can take as end-members. Our interest of applying such an analysis was not to provide accurate spatial representations of mixing spatial and temporal processes, but to provide an adequate estimation of them with few input parameters. Bearing this in mind, we tried to perform an analysis with the least possible number of end-members. In our sites the potential end-members we had according to available data are: river water, groundwater in agricultural areas, lateral stream water and irrigation channel water. Rainwater was not included as an end-member because it was considered that it does not impact directly in the hydrodynamic of the riparian aquifer. In fact, the volume of rainfall over the riparian aquifer is insignificant compared to that coming from the feeding areas. In Bidasoa site, where the volume of rainfall is important and the aquifer has not lateral continuity (figure 2), the semi-confined behavior of the aquifer limits a lot the influence of rainfall. We applied the method in a monthly scale, as it is the scale of the sampling. The results from PCA analysis and the site-specific attributes were used to choose the simplest end-members in each site. In this way special attention is paid to electrical conductivity (EC) as it can potentially differentiate end-members, namely river water and groundwater (Jencso et al., 2010).

Using the EC of the end-members as a reference, the percentage of water coming from each of them in all the monitoring points of the aquifer was estimated. Taking the results obtained from this approach into account, the theoretical concentration of NO_3^- and DOC for each control point was calculated using the following equation:

$$[TC]i = (\%R*[C]R) + (\%Aq*[C]Aq), \text{ (equation 1)}$$

where [TC] is the theoretical concentration of NO_3^- or DOC, % is the percentage of water from each end-member, and i, R and Aq are the control point considered (i) and the end-members (usually the river and the aquifer). Once the theoretical concentrations were calculated, they were compared with the real concentrations ([RC]), obtaining the rates of variation, Δ (delta), which are mapped in Δ-maps for each month in each site. For this purpose, spline analysis of interpolation was performed using ArcGIS 10.1. In places where Δ is negative there is a depletion/consumption of these compounds, meaning that attenuation processes might be taking place at these points. In places where Δ is positive, there is an enrichment/increase of those compounds, so a point-source input might be contributing to higher concentrations. $\Delta C = ([RC]i - [TC]i)/[TC]i$.

3. Results

3.1. Hydrology

Figure 3 shows the daily average discharge in the gauging station of each study site. Monthly and quarterly sampling campaigns are indicated with circles and arrows respectively. In addition, discharge needed to start flooding and flood around the 50% and the 100% of the floodplains are shown. These data are not shown for the Tagus River as this is a highly regulated river where discharge barely shows any variation and flooding situations do not occur (Bodoque et al, this issue). Beginning of flooding was established in 600, 150 and 1000 m^3/s for Ebro, Bidasoa and Garonne, respectively, resulting in 10, 7 and 5 the events in which the water from the river starts flooding the forest next to the river (figures 1 and 2). For an event that would flood around the 50% of the floodplain 1100, 250 and 1400 m^3/s thresholds were set, with 3, 2 and 4 events (figure 3) flooding mostly forest (riparian or poplar) in Ebro and Garonne sites and forest and agricultural areas in Bidasoa. From discharges of 1400, 400 and 2800 m^3/s upwards for the rivers Ebro, Bidasoa and Garonne, respectively, it is considered that almost all the floodplain area is flooded. Looking figure 3 only one event exceeded that threshold in each site reaching the agricultural area in all of them (figure 1). From these data it can be said that Ebro is the site where the forest is flooded more often and Garonne the site where a great part of the floodplain is more frequently flooded.

In the figure 3e the autocorrelation functions of average daily discharge of the rivers can be observed. The function for the Tagus River shows a very gentle decreasing slope due to its high regulation. In the case of Ebro, this function shows a gentle decreasing slope which is related to a high dependency of eventual discharge on previous discharge and so, to a slower response of discharge during events (a certain level of regulation). This slower response would result on events of a longer duration. This is also observed in figure 4 being Ebro the site that shows a bigger area in the graph between the two lowest thresholds of flooding. The autocorrelation function for discharge of Bidasoa and Garonne (figure 3e) diminishes more rapidly and reaches the r = 1.5 level in half of the time than in Ebro. In these cases, a certain discharge has a lower influence on subsequent ones and flood events will last shorter. However, in Garonne more than half of the time floods cover a higher extension of the floodplain (around the 50 %) (figure 4). In this case higher increases in water level are needed to start flooding due to the higher incision of the river. Finally, Bidasoa is the site that shows a lower extension of floods as most of the time is only the forest line next to the river the flooded one. In this site the river incision is quite important so high water levels are needed to get water in the floodplain. However, once the line of forest is overflowed, a great part of the floodplain can be flooded.

3.2. Hydrogeology

In figure 2 landscape differences between study sites have been represented. Concerning the influence of the river in the aquifer two recharge types were considered: on one hand the vertical recharge when flooding and on the other hand the two-ways water exchange between river and aquifer (lateral connectivity), the last is very clear mainly in Garonne (Sun et al., 2015) and Ebro sites. Additionally, the water level variations in both the river and the piezometers (near river, intermediate and distant zones) were indicated. Except in Tagus site, where water table only fluctuates during irrigation period, in the other sites water table temporal evolution in different piezometers is quite similar (figure 3), and similar to the discharge evolution in the river. The average depth of the water table (figures 5 and 7) ranges from around 2 m (Ebro, Tagus) to 5 m (Bidasoa) being an increase in depth from the near river zone toward the distant zone in Ebro and Tagus sites. In the other two sites spatial distribution is more homogenous being the water table depth 4.5-5 m in Bidasoa site and 3.5-4 m in Garonne site, in this case with a high temporal variation.

With regard to water table fluctuation boxplots in figure 7 show differences among the sites. The biggest variation is observed in Garonne site where water level fluctuates up to 6 m as much in the near river as in the distant zone. In Ebro site the fluctuation is also important, up to 3.5 m, being quite homogenous spatially. However, in Bidasoa site the variation is smaller, around 2-2.5 m, but homogenous also. Finally, Tagus site shows the smallest fluctuation, around 2 m in both extremes of the meander and 1 m in the middle. Figure 5 represents the percentage of time (day) that groundwater level is below a certain depth. All of the piezometers in each zone (near river, intermediate, distant) show similar responses, so only one was selected to make the figure.

In Ebro site water level in the three zones is above terrain level in a small percentage of time (6% in near river area, 3% in the intermediate zone and 0.7% in the distant zone), as it is shown by the negative water depths. This situation of total saturation of soils happens during flood events, and is supported by the two recharge types above mentioned. In Garonne site the situation is similar but with lower percentages of flooding time in the near river, 2.5%, and the intermediate (0.9%) zones; for the distant zone is similar of that in Ebro site (0.6%). In Bidasoa site daily mean water depth did not reach terrain level during the studied period even if there were some events that flooded part or the entire floodplain (figures 3 and 4). However, water level was eventually near the surface, to less than 1 meter 0.4 % of the time in the near river and intermediate zones and 0.7 % in the distant zone (according to Gold et al., 2001, substantial groundwater denitrification has been found where the water table was within 1 m of the surface). In Tagus site water level was more than 2.5 m deep from the terrain surface during the entire study period.

Figure 6 shows flow nets in two hydrological situations which correspond to the usual low and high water level periods (flooding situations are not represented). An overall view of the figure allows making a distinction among the flow nets. The flow in Tagus site is radial with groundwater going from the internal part of the meander (more irrigated area) toward the river all along its course. However, in Ebro the flow is more or less parallel to the river with a clear influence of the river water in the aquifer. In the other two sites the flow presents an intermediate net, mainly in Bidasoa site where some flows change their direction depending on the hydrological situation (more radial from the alluvial fan in high level periods; more parallel in low level periods). Hydraulic gradient (m/m) in a given situation hardly changes along the site. During low level periods is between 0.001 (Ebro) and 0.003 (Garonne and Bidasoa) and in high level periods between 0.002 (Ebro) and 0.004 (Garonne and Bidasoa). In Tagus site, due to its specificity, gradient is very low and practically constant in the river near zone (0.0002-0.0006) but increases greatly towards the center of the meander (0.007).

3.3. Hydrochemical characterization

Figure 3 indicates the moment of the monthly (circles) and quarterly (arrows) sampling campaigns and figures 7 and 8 show the hydrochemical characterization in each of the study sites. In boxplots in figure 7 the variation range of the most significant parameters can be observed. Sulphate and alkalinity have not been included because, generally, their spatial evolution is similar to that of the electrical conductivity (EC). Sampling points in the aquifer have been grouped according to their distance to the river and results for those groups and for the river are shown separately in the figure.

3.3.1. Principal Component Analysis

In order to make visible the different groups of waters a factor analysis was performed, for each of the sites. It was intended to better understand river-aquifer connectivity and mixing processes in the sites. Considering the first four principal components (PCs) between 66% (Tagus) and 76% (Ebro) of the variance of the data matrix is explained (figure 8). As observed in this figure water types are distributed between two parameter groups: in one of them EC, Cl^- and SO_4^- are found and in the other pH and O_2. This distribution helps establishing differences between groundwater and river water. In addition the location of waters from different zones of the riparian area in these PCAs gives an insight on hydrochemical spatial evolution.

Third and fourth principal components (less than 15% of variance) are related to site-specific environmental conditions which affect biogeochemical processes controlling nitrogen compounds fate, oxidation-reduction conditions and temperature. Only in Bidasoa site PC3 (15%) shows a clear loading for nitrate and sulphate, which is indicating the influence of the limited (intermediate zone) agriculture activity in the site.

3.3.2. Principal Component meaning

Figure 7 assists in interpreting the meaning of the PC axes. High EC, related to chloride, sulphate and alkalinity, is clearly located in the agricultural area in Ebro site and values decrease towards the river. In Garonne and, mainly, in Tagus sites distribution is different, being the intermediate and near river zones the ones with the highest values. This difference can be explained in Tagus site by the intense application of fertilizers in the lowland area; the distant zone is closer to the irrigation channel and directly affected by its waters, so that fertilizer loading is not as high as in the lowland. In Garonne site explanation can be related to the biological activity in the floodplain which would be the source of an increase in alkalinity observed in this site. In Bidasoa site the highest values of EC and alkalinity are related to the farm; in any case values of EC, alkalinity and sulphate in Bidasoa site are always lower than those in the other sites.

Concerning dissolved oxygen (O_2) the highest contents (average higher that 85%) are always in river water, but also in the distant zone in Tagus (due to the channel) and Garonne (irrigation). In both cases the lowest contents are in groundwater in the near river zone (around 20%). Similar to those are the values in the three zones of Ebro site. Slightly higher (30-37%) is the content in the riparian zone of Bidasoa site, except for groundwater near the farm where the content is lower (18%). Spatial distribution of pH (no figure) is quite similar to that of the O_2, with the highest values in the rivers, between 7.7-8.7, and the lowest ones in groundwater in the riparian zone (6.0-6.8).

With respect to other variables involved in nitrate attenuation (DOC, ORP and N-compounds) factors controlling them are site-specific so that their spatial distribution is quite different among sites. As can be observed in figure 7 the main DOC source in Bidasoa site is the farm (5 mg/l on average) and in Ebro site the agricultural input is very obvious, around 14 mg/l, being in both cases the river the point where the lowest values are measured (2-3 mg/l). However, in the other two places the main source of DOC is the river (6 and 2 mg/l in Tagus and Garonne sites, respectively). In Tagus site, where DOC has a strong loading in PC1, there is a small increase in the distant zone which should be related to the influence of the irrigation channel. Rivett et al (2007) stated that DOC levels in most aquifers are relatively low, < 5 mg/l, which is in accordance with our data except for Ebro site where intense irrigation makes the values to be higher in groundwater.

Regarding Oxidation Reduction Potential (ORP), presented in PC3 and PC4 (no figure), the highest values and the ones with a higher variation range are observed in Garonne site (figure 7) with values between 180 and 230 mV and a decreasing trend from the agricultural area to the river. The other sites show a range between 75 and 150 mV without any significant spatial trend. It is to be pointed out the distant point in Bidasoa site, next to the farm, where groundwater shows negative values of ORP. These come along with the highest values of alkalinity, DOC and ammonium and the lowest of O_2. Negative values of ORP are also observed exceptionally in some places of Tagus site.

N-compounds occur in different forms according to sources considered. In all the sites, except in Bidasoa, the majority of N is found as NO_3^-. The highest concentrations appear in groundwater of the agricultural area (32 mg/l in Ebro site and 62 mg/l in Garonne site, on average; in both nitrate comes along with high values of EC, SO_4^{2-}, K^+ and SiO_2 and is well represented in the first two components, figure 8) and the values decrease towards the river, mainly in Garonne. In Tagus site spatial variation is not so evident but a little higher concentration (35 mg/l) is observed near the river as a result of the intense use of fertilizers in this area. In Bidasoa site the most significant source of pollution is the farm, being the principal N-form released ammonium (up to 36 mg/l NH_4^+ in piezometers near it, distant zone, and NO_3^- below 1 mg/l); in fact NH_4^+ shows a high loading in PC2 in this site (figure 8). Another source of N is related to agricultural practices in the intermediate zone though they are not very important; this is why a small increase in NO_3^- values (12 mg/l) is observed in piezometers near river. Nitrate in rivers range from 13, in Garonne, to 3 mg/l, in Bidasoa site.

Silica shows a similar pattern in all the sites with values ranging from 10-20 mg/l of SiO_2 in groundwater (mainly in the distant zone) and up to 4-6 mg/l in rivers. Silica is thought to be a lithological signature due to the significant positive correlation with EC, sulphate, alkalinity and water depth and negative one with dissolved oxygen and pH. Silica is also well related to nutrients as nitrate and potassium in Garonne and Ebro sites where agricultural practices in distant zones are well defined; however, such a relation does not appear in the other two sites because these practices are either limited (Bidasoa) or uncontrolled (Tagus). Groundwater average temperature ranges between 13 and 16°C in Ebro, Garonne and Bidasoa sites (figure 7) being the temperature in piezometers near the river in the lowest part of that range. In Tagus site temperature is a little higher (around 18°C) with slight differences between places. River water average temperature is around 13.5-15°C, except in Tagus where it is higher (21°C) and more variable along the year (25°C fluctuation) as a result of being a much regulated river.

3.3.3. Hydrochemical spatial evolution

In figure 8 waters of different zones (river, near river, intermediate and distant zone) are gathered according to their location in the I-II factorial plane of the PCA. Arrows show groundwater flow from distant zones to the river as well as connection between aquifer and river. Diagrams of Garonne and Ebro sites depict similar hydrochemical evolution. In both places groundwater in agricultural area (distant zone) is characterized by NO_3^-, EC, Cl^-, SO_4^{2-}, and SiO_2, being here where the water is deeper (wd). In Ebro site DOC content is also significantly high in the agricultural zone. Moving towards the river values of those elements significantly decrease in Ebro site, whereas in the Garonne site slightly decrease. In both sites concentrations are the lowest in the river, except for O_2 and pH (also DOC in Garonne). Groundwater in intermediate zone of both sites occupies a broad space in the graph showing important hydrochemical variability ranging from hydrochemical composition of waters in distant zone to that of waters in near river zone. In Ebro site near river zone waters and distant zone waters appear more separated that in Garonne site, showing a clearer trend along the flow direction (figure 6). In any case, river waters always appear sharply separated from groundwater but close to the near river waters indicating a probable connectivity.

In Bidasoa site the farm (distant zone) significantly influences hydrochemical evolution along the flow direction (figure 8) so that waters near the farm are clearly separated from the others. These waters are characterized by high values of DOC, Cl^-, ammonium, EC and alkalinity (usually with negative values of ORP). In this area the water level is quite deep. Downward nitrate and sulphate contents increase due to nitrification and leaching of fertilizers applied in the intermediate zone so that the effects are more relevant near river. SiO_2 also shows an increase towards the river what is to be related to water coming from the lateral stream that drains granites and shales; in fact this lateral water enters into the aquifer deeply (bedrock is 25 m deep) and flows upward near the river (figure 2). Finally, river waters are characterized mainly by high values of dissolved oxygen and pH (as are the ones in the stream). As a result waters in this site are well distributed along the flow pathway.

Surface lateral flow is also present in Tagus site where a channel derived from the river is used for irrigation. So waters in both river and channel show similar characterization with high values of DOC, O_2 and pH. From the channel downward there is a progressive increase in EC, Cl^-, SO_4^{2-}, alkalinity, SiO_2 and NO_3^- as fertilization is very intense (Bodoque et al, this issue). The broad spatial variety of agricultural practices in this site makes practically impossible to establish a suitable relation between causes and effects on the basis of available data, which derive from a monitoring design that has been satisfactory to assess the main hydrochemical aspects in the other sites. Even though flow net in this site is very simple (figure 6), with a radial flow toward the river and without connectivity between aquifer and river, there is not a clear hydrochemical pattern being the groups in the graph (figure 8) quite mixed. Thus, river water group is not clearly separated despite the lack of influence of the river into the aquifer.

3.3.4. EMMA application

A simple end-member mixing analysis was performed to estimate proportion of water from different sources in the mixed water of the aquifer. Our approach is based on the PCA results, being the main goal to provide an adequate estimation of the mixing with few input parameters. Having this in mind, we tested the potential use of the electrical conductivity (EC) as a simple good indicator of water mixing. In fact, EC has a strong loading in the PCA performed in each of the sites, it is highly correlated with many of the other parameters, as sulphate, calcium or sodium, and especially chloride, except in Bidasoa. Using EC the percentage of water coming from each of the end-members in all the campaigns and the monitoring points was estimated. Δ-maps have been derived to localize the attenuation zones.

As shown in figure 7, EC separates well groundwater in agricultural zones and surface water in both river and stream (Bidasoa) or channel (Tagus). According to spatial evolution (figure 8) an analysis with two end-members was applied: surface water (SW) and groundwater (GW). In Garonne site SW and GW sources were clearly identified (on average 250 and 1000 μS/cm, respectively), as well as in Ebro (750 and 3200 μS/cm). In Tagus site (1900 μS/cm in the channel and 2500 in agricultural areas) the situation is more complex being multiple fertilizers poured lowland in the meander; in spite of this an attempt was made considering the channel as the SW source. This approach does not work in Bidasoa site owing to the disturbance created by the point-source of pollution, so that we were obliged to use three poles and, consequently, two chemical indicators (alkalinity and silica). In fact, in Bidasoa apart from the river pole (the lowest values) water spreading from de farm (high alkalinity, around 5 m/l), in a radial flow net, and water coming from the lateral rocks (high silica, around 10 mg/l) are also considered.

Figure 6 shows the overall results of river water contribution to the aquifer obtained from EMMA analysis and along with figures 2 and 3 help showing the river-aquifer relationship. In Garonne site during flood events, which only happens for a few days, the river water level increases rapidly and water flows into the floodplain allowing the lateral (water infiltration through the river bank) and vertical (flooded water percolation) recharge of the aquifer. Despite there being no observations during the flood itself, the part of the river water in the meander a few days after the flood, during high water level conditions, estimated from EMMA, ranges from 75% upstream next to the river to 0% northward and in the agricultural area. During the drying stage the water flows back into the river, and three months after the flood, during low water level conditions, the percentage of water from the river in the meander is only between 45% in a small area near the river and 0% in more than half of the aquifer. The fact that this proportion of river water is lower downstream to the north of the aquifer is in accordance with the hydraulic heads showing a more significant flow from the aquifer to the river in the northern area. Finally it seems that the water in the aquifer always contains a proportion of river water in the upstream part (southern part of the meander) where the flux of water flowing back from the aquifer is very small.

In Ebro site during the low waters period the river and the aquifer have similar water levels, and flow direction is quite parallel. There is a backflow entrance of water in the aquifer from the river that matches its previous course. Otherwise, during the high water period this backflow is compensated with the entrance of river water at the meander head, being the previous river course a preferential path for the groundwater. During flooding situations the aquifer receives lateral and vertical recharge. The river water in the floodplain aquifer is always very high, up to 80% in near river zone and in a part of intermediate zone during low level periods, and up to 90% in high level ones.

In Bidasoa site, during high flow periods surface water from the lateral stream prevails. This enters the aquifer through the alluvial fan (the highest hydraulic head), where the farm is located, and it moves mainly northward where its contribution reaches a 60% in the aquifer. In these periods the Bidasoa River contribution is small (10%) and spatially limited to the south part of the meander. However, during low flow periods there is a higher entrance of water from the river in this part, up to 70%, going this percentage decreasing from south to north at the same time that lateral contribution goes increasing. The floodplain is rarely occupied by the river and the main recharge of the aquifer is coming laterally from both river and stream, being the vertical recharge very reduced and delayed after flooding. Finally, in Tagus site there is not a two-way water exchange between the river and the aquifer. Entrance of surface water in the aquifer is addressed with the irrigation from the channel which is a diversion of the river. Water coming from the channel can represent up to 60% in some areas but is very variable from one point to another.

The results obtained from EMMA analysis, the percentage of water coming from each end-member during each sampling campaign, together with the observed NO_3^- concentrations in those points, were used to estimate the theoretical values of NO_3^- in the sampling points of the aquifer by means of the mixing approach described in equation 1. These theoretical NO_3^- concentrations should be near to the observed ones in the cases when water mixing was the only process involved. Those theoretical values were compared with observed NO_3^- values in order to detect areas where an increase (positive Δ; external input) or decrease (negative Δ; attenuation processes) of NO_3^- was taking place. Figure 9, shows areas that permanently along the year show negative ΔNO_3^- and, as a consequence they are considered to be permanent hot spots of nitrate attenuation.

4. Discussion

Some studies, reviewed by Burt et al (2013), point to the high degree of variability of factors accounting for the attenuation processes among sites in a riparian zone and a limited predictive capacity based upon broad-scale drivers. Now we discuss the results obtained in the four riparian zones in order to identify the main factors involved in nitrate attenuation zones and delimit the places where attenuation processes are more evident along the water flow and try to identify and justify their spatial location. Potential zones of high attenuation rates are identified where nitrates concentrations are high and available dissolved organic exist in a context of anaerobic conditions.

4.1. Hydromorphological control

For Tagus site, totally controlled by a dam upstream, the consequences of no hydraulic connectivity between the river and the alluvial plain is there are no natural decontamination zones for nitrates (Bodoque et al., this issue). On the contrary, Ebro site is the most efficient and also the most dynamic in terms of hydraulic connectivity between the river and the riparian zone. Hence, connectivity upland-river-aquifer is a key point. Hydrochemical data can help us understand hydrological information. So, figure 8 shows the spatial evolution (from the distant zone to the river) of water characteristics based on PCA analysis of available data. Such a distribution allows tracking the main processes taking places in the sites. We have roughly marked on the figure the domain where surface water (SW) should be affecting groundwater (GW) chemistry. The fact that some points of SW remain out of this domain indicates specific time situations when such affection is not happening. Nevertheless our interest is in the overall conceptualization.

Diagrams of Garonne and Ebro sites depict similar evolution from the agricultural area to the river. This is a result of being the land use zoning very clear with the agricultural practices being limited to the distant zone. In Ebro site near river zone and distant zone (agricultural area) waters appear more separated which can be explained by the flow net prevailing in each site (figure 6). In fact, in Ebro site river water enter the aquifer and flow all along the near river and intermediate zones making characteristics of waters in these zones to be closer to those in the river. However, in Garonne groundwater flow is more radial from the distant zone so that characteristics of groundwater are more homogeneous and clearly separated from the river water even though entrance from the river become very important in some periods in the upstream part of the meander (figure 6).

Also in Bidasoa surface waters and groundwater are clearly separated. The more radial character of the flow net does not allow the river water presence in the aquifer to be continuously significant in the riparian area. Entrance of water from the lateral stream becomes more important in some periods, nevertheless groundwater show very different characteristics as this water intersects the pollution point source. Consequently, waters of different distances from the river occupy different positions in the graph (figure 8) making very evident the influence of the farm on the overall hydrochemical behavior in the site. Water samples positions in the graph (figure 8) shows a messed spatial distribution for Tagus site which is in agreement with the different types of agricultural practices, some of them very localized in space and time, and with an uncontrolled use of a great variety of fertilizers. In this site surface waters appear near aquifer waters in distant zones from the river, but without really indicating direct connectivity with it. Irrigation with waters from the channel derived from the river explains this proximity.

Principal Component Analysis provides a good overview of the different types of waters in a riparian zone, being considered it is based on a detailed monitoring in both space and time. However, interpretation of the spatial evolution may not be so obvious to do, as site-specific factors might?? need to be taken into account. Similarity of hydrochemical characteristics can lead to erroneous understanding of the connectivity with the river. On the other hand, a certain degree of connectivity may remain hidden if data are not adequate to represent site-specific factors. In any case, hydrochemical data have to be interpreted together with hydrological observations. The connectivity is depending on hydrology and geomorphology: the meander form and river water level are controlling the lateral physical exchanges between surface water and macro-porous media, whereas the hydrology is controlling the over-flood coupled to morphology of alluvial plain.

Flooding enables the percolation of DOC from soil and its rapid incorporation to the aquifer due to the high permeability of the alluvial deposits. It is the case in Garonne site where DOC enters the aquifer both laterally from the river (when river discharge is rising) and vertically when flooding. Nitrate input is guaranteed by the lateral continuity of the alluvial (fig. 2), with a continuous flow from the agricultural area. In this area it is not expected to be high attenuation of nitrate as low DOC and high O_2 concentrations in groundwater are far from required (fig. 7). Water table fluctuation, which is very high (figure 7), is controlled by the river (horizontal exchange of water) due to the important river incision and the limited thickness of the deposits. Figure 9 summarizes the main sources and pathways of nitrate and carbon. Continuous input to the marked attenuation zone (permanent negative ΔNO_3^-) is guaranteed by both the aquifer (N) and the river (C), though the attenuation processes become most important in flooding situation (DOC percolation from soil) when these processes could take place also in the north half of the site.

For Ebro site, the small river incision and the gentle slope of the floodplain make the flooding to occur (figure 4) more frequently and with a longer duration. Additionally, the extensive riparian corridor is dominated by forest. Both aspects favor organic carbon from the soil to enter the aquifer and add to the DOC coming in groundwater from agricultural land that also shows high NO_3^- content (figures 7 and 9). Nonetheless, the presence of DOC coming from soil in the aquifer seems to be delayed because as figure 3 shows periods with positive ΔDOC in the aquifer occur time after flooding situations. Water table in the corridor (near river and intermediate zones) remains over the land surface around a 5% of time (18 days a year), longer than flooding time of the 50% of the site which is 2% (figures 4 and 5). Apart from this, water table fluctuation is relatively small (compared to Garonne site; figure 7) and similar in all the zones of the site. It means water table dynamics is mainly controlled by the aquifer, which has a high lateral continuity and a big thickness (figure 2).

As mentioned for Garonne and Ebro sites, in Bidasoa it has to be also considered the input of DOC by percolation from soil when flooding, even though the forest area is just a narrow strip along the river course. Such an event occurs in this zone occasionally, with lower duration and extension than in the previous sites (figure 3). Despite it, the water table remains deep and hardly reaches the topsoil (2 days a year) never rising above soil surface (figure 4). This is due to the semiconfined character of the aquifer, with a thick silty formation overlying the highly permeable gravel deposits. However, this situation can help the upper part of the terrain maintain high water content for a long period of time. Consequently, water percolation from the soil, including DOC, is limited and delayed in time, so that the most important input of DOC is from the farm according to the flow net (figure 6). On the other hand, water table fluctuation is quite similar in different strips from the river (figure 7), being the more distant where the table is shallower. Taking also the important incision of the river into account it is concluded that the water table in this riparian area is mainly controlled by the lateral stream conducting its water into the aquifer, in a radial way in high level periods (figure 6).

4.2. Nitrate attenuation rate control

In Garonne site negative ΔNO_3^- was observed in groundwater all along the floodplain, which could be related to attenuation processes by denitrification. DOC has two main sources in this site: the river (figure 7) and the organic matter-rich top layers of soil. In fact (figure 3), positive ΔDOC appears in groundwater during and just after important rising of the water table (mainly in winter and spring) during which the table reaches topsoil. Water level evolution in the aquifer is similar to that in the river so that the highest rising situation coincides with flooding in the area. Indeed a half of the site is flooded during a percentage of time (2%, around 7 days a year) similar to the time during which the water table remains over the land surface in the near river and intermediate zones (figures 4 and 5), covered by forest. Despite the low duration of floods, they cover a high extension due to the flat topography (figure 2).

In Ebro site negative ΔNO_3^- was observed in groundwater anywhere along the riparian area. Attenuation rate is high any time in the near river zone (up to 90%) but it is also important in the intermediate zone (up to 50% in high level periods). This fact has to be partly related to the river water presence (figure 6) which is always very high in these zones, supported by the prevailing flow net, parallel to river. The old course of the river, filled of coarse gravels, helps this pattern. The river is one of the sources of nitrate in the riparian zone as the concentration in the river water is relatively important, higher than in the Garonne and Bidasoa rivers (figure 7). Anyway, the most important source of N is the agricultural area (distant zone). According to the flow net, nitrate-rich groundwater flows towards the down part of the meander. On the other hand, the main source of DOC is also the agricultural area, so that N and DOC share the same source. Furthermore, concentration of DOC is quite high compared with agricultural areas in the other sites (figure 7). This fact is to be related with an intense irrigation and a high content of organic matter in the soils. Therefore it could be thought of the possibility for nitrate attenuation processes to take place in the agricultural area before groundwater reaches the riparian zone (dissolved oxygen content in the agricultural area is low, figure 7, and could help these processes). Unfortunately the monitoring points of the agricultural area were located just in the limit with the riparian zone, so that we cannot consider processes potentially occurring in the distant zone itself.

In Bidasoa site the most important source of N is the farm where a high amount of NH_4^+ is introduced into the aquifer and moved according to the flow net (figure 6). Most of it is transformed to nitrate when travelling towards oxidizing environments. In fact O_2 in groundwater near the farm is very low, the lowest among the control points in all the sites (figure 7). This is the reason why total inorganic nitrogen ($NO_3^- + NH_4^+$) was considered when calculating ΔNO_3^- in this site. Attenuation is evident in groundwater all along the site with rates usually around 50-75%. Nitrate enrichment is observed punctually after high water table periods but only in points near the reduced agricultural area (intermediate zone). Concerning DOC the main source is also the farm, so that the highest amount of N and C are coming from the same source. In general, there is no positive ΔDOC along the riparian area as groundwater in the farm has been considered as a pole in the EMMA analysis. Nevertheless, occasionally in time and punctually in space, positive ΔDOC were observed after important floods (figure 3), which means that this analysis, as we applied it, cannot be used to understand specific situations. Negative ΔDOCs, up to 75%, are placed mainly along the flow lines from the farm.

4.3. Efficient zone delimitations

We discuss the results obtained emphasizing the spatial dimension of the attenuation processes regarding nitrates. Figure 9 shows the places where usually these processes happen along the year. N and C main sources are also shown for a better understanding of the involved dynamic.

As observed in figure 9 for Ebro site, the most permanent attenuation zone is located in the near river and intermediate zones downstream in the meander where favorable conditions take place. The figure gives a general explanation of the processes considered. N and C inputs (agricultural areas) converge in this spot of shallow water table where additional DOC supply could be expected when flooding.

In Garonne site, it appears that the most active nitrate attenuation area is located in the central part of the floodplain, with rates usually higher than 60% (even higher in high level periods).

Attenuation processes in this area can be enhanced by the most important nitrate flux from the aquifer and by high DOC availability due to the low topography which makes flooding easier. For Bidasoa site, figure 9 shows the location of the most permanent attenuation zone. This spot is conditioned by the position of the farm and the flow pattern. In fact, all the zones of the aquifer which are not in the flow path from the farm show quite good quality water since surface water entering the aquifer (from both the river and the stream) are of relatively good quality. We cannot refer to the potential attenuation processes in these zones as not mixing with polluted water occurs there. But we can at least delimit the attenuation zone regarding the actual pollution source.

In Tagus site Δ-maps are difficult to understand due to the complexity of the performed analysis. Information on this site has been treated by Bodoque et al. (this issue) showing the difficulty to integrate different approaches (hydrochemistry, potential denitrification, bacterial and macroinvertebrates indicators). Focusing on our interest, punctual patches of positive ΔNO_3^- appear during the irrigation period, which is related to the uncontrollable use of fertilizers and the broad variety of agricultural practices. This makes it practically impossible to establish cause-effect relationships with our data. In fact, unlike in the other sites in this one N inputs can occur everywhere as agricultural practices cover from the distant zone to just the river. Negative ΔNO_3^- predominate, from 20 to 60%, showing a high irregular spatial distribution. This fact is also visible in ΔDOC maps. Only some enrichment patches of DOC are observed, without any temporal trend. Negative ΔDOC can reach up to 50% in the internal area, during irrigation period, without any spatial pattern. As observed in figure 7 the main source of DOC is the river. However, no river water enters the aquifer (figure 2) and no flooding situations occur (figure 4). However, water used for irrigation is tapped from a channel diverted from the river (figure 6) which allows DOC to reach the aquifer by irrigation. Attenuation spots (figure 9) are limited to some patches in the intermediate and near river zones. Bodoque et al. (this issue) have shown the importance that recovery of flooding situations will be in order to activate ecological functionality.

5. Conclusions

A comparative study of four riparian areas in the SUDOE region (Southwest Europe) was conducted, regarding their capacity for nitrate attenuation. This in mind we focused on several site-specific factors controlling N and C sources, flow net and the location of attenuation zones. Taking into account the first objective of this paper the simple approach applied in this study (based on data analysis, PCA, EMMA), resulted in a useful tool for the spatial delimitation of the zones where permanent nitrate attenuation processes take place in riparian areas. A monthly based one year monitoring, in both the river and the aquifer, in increasing distances from the river, allowed having an overall conceptualization of the attenuation processes, assuming that usual high and low level periods were monitored. Due to the inherent difficulty for sampling during short flooding events the continuous monitoring of the water level in the river and the aquifer becomes very helpful for further knowledge.

As it has been observed, attenuation processes can occur in a riparian area even though connectivity with the river is temporally limited, given other factors (N and C sources, superficial lateral flows, aquifer flow net) favoring these processes take place in that area. However, this simple approach may be difficult to apply in areas where pollution sources are very diverse in type and in both time and space, as is the case of Tagus site. This leads us to conclude that a general conceptual model cannot capture all the factors needed to understand the nitrate removal dynamics of a riparian zone, putting in evidence the importance that the knowledge of site-specific factors has. Nevertheless, the methodology followed in this project enables the delimitation of the permanent attenuation zones in a site and helps specify a more focused research that would be developed in those zones.

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Figure captions

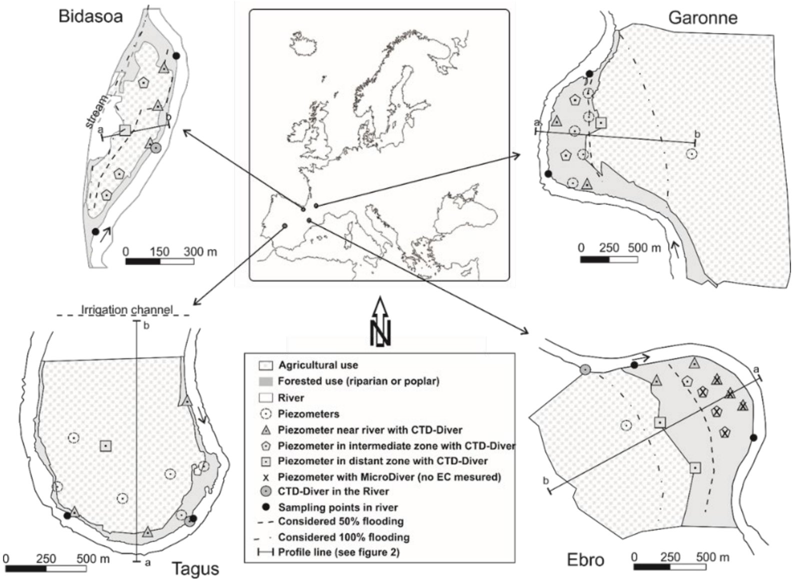

Figure 1: Four study sites location, land uses and monitoring network (modified from Español et al., this issue).

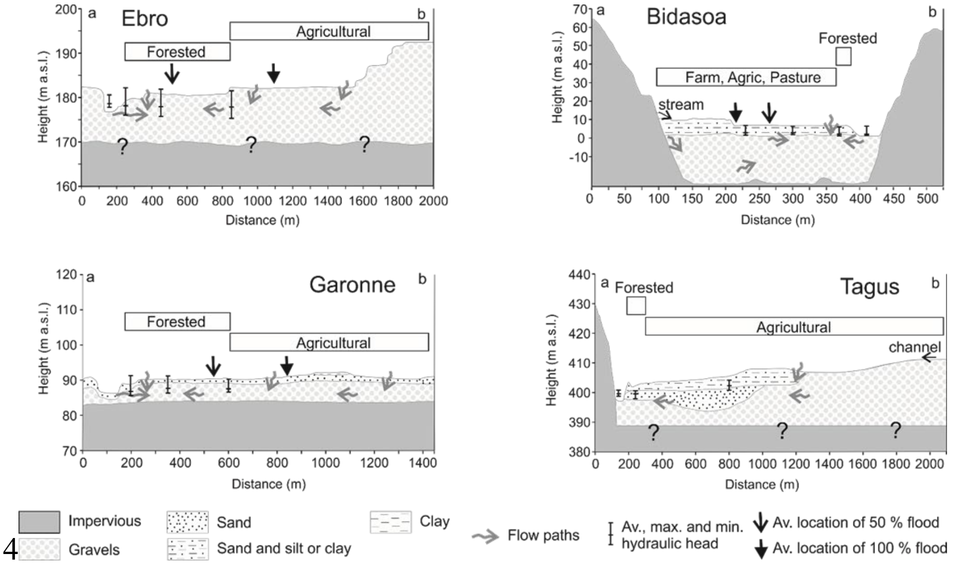

Figure 2: Four study sites geology and landscape. Hydraulic head variations along the site are also represented.

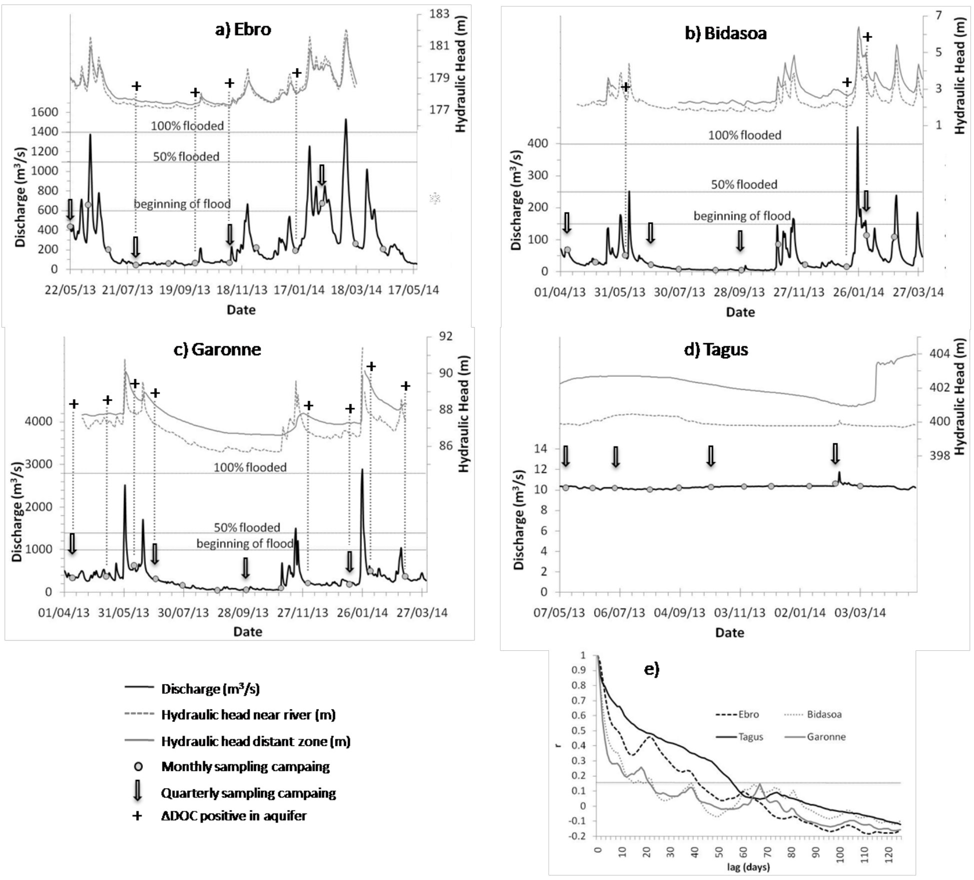

Figure 3: a-d) Hydrographs and piezographs registered in the studied sites (2013-2014). Sampling moments are also marked. e) Autocorrelation functions of the four rivers for the same period.

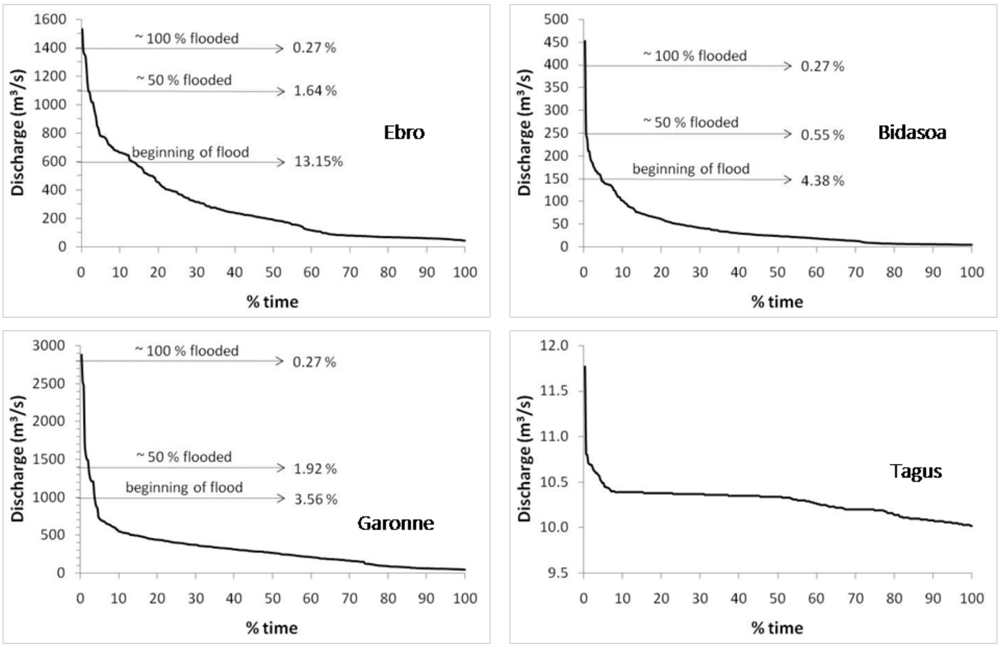

Figure 4: Flow duration curve of the four rivers. Different flooding level thresholds are marked.

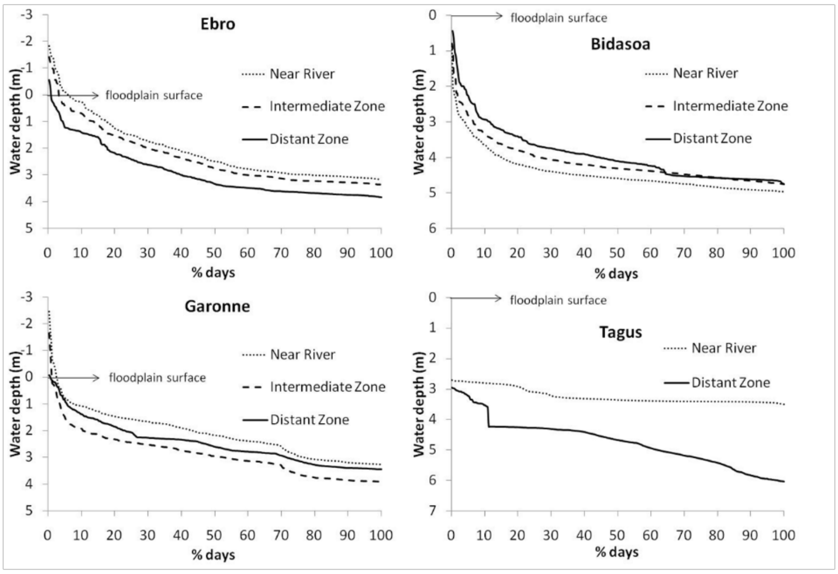

Figure 5: Percentage of time (days) that mean daily (continuously registered data) water depth in the aquifer is above a certain level (considering floodplain surface as 0) in piezometers of the near river, intermediate and distant zones of the study sites.

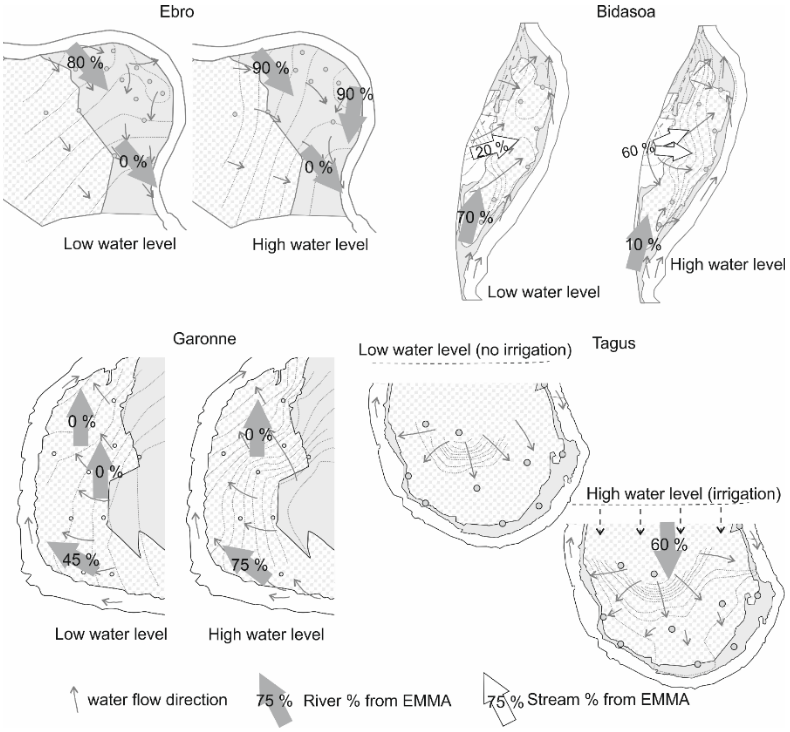

Figure 6: Flow nets of the study sites. Water high and low level periods are considered separately. River water percentage in the aquifer (obtained from EMMA analysis) is also shown. In Tagus site the water level in the river barely changes, so that, high water levels are related to high water levels in the aquifer during the irrigation period.

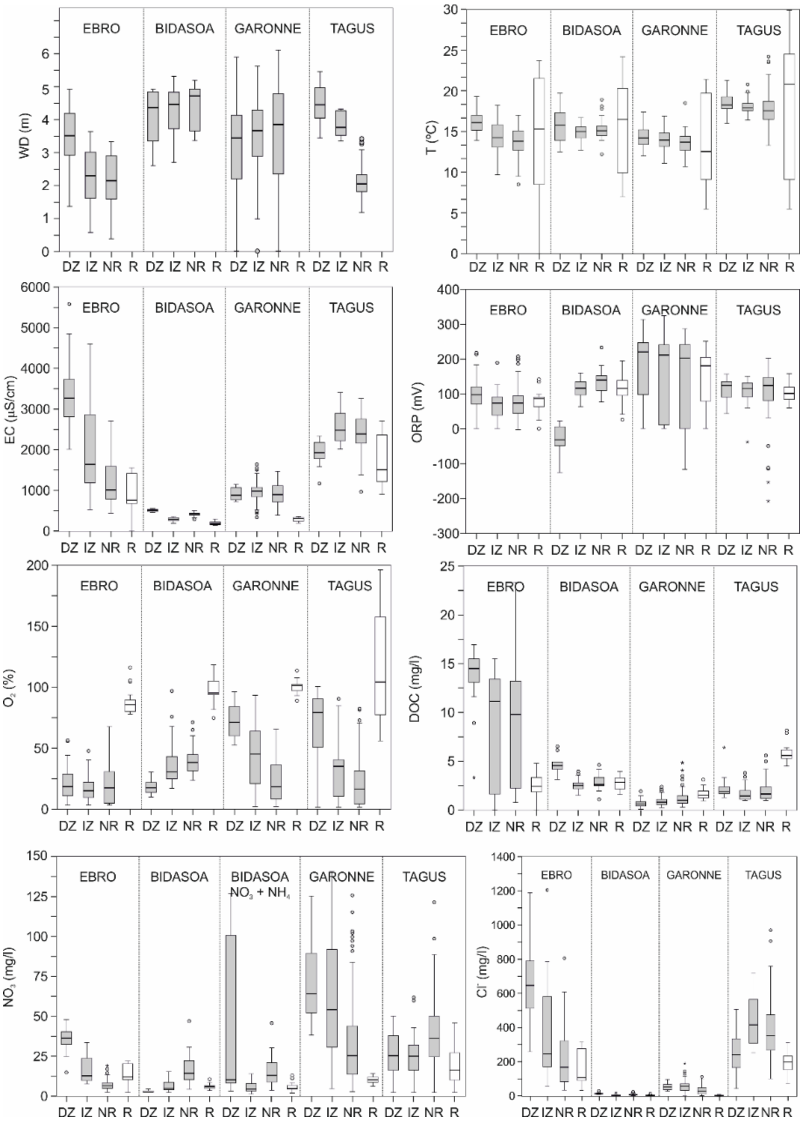

Figure 7: Boxplots of some important physicochemical indicators based on monthly sampling data. Distant zone (DZ), intermediate zone (IZ), near river zone (NR) and river (R) are considered separately.

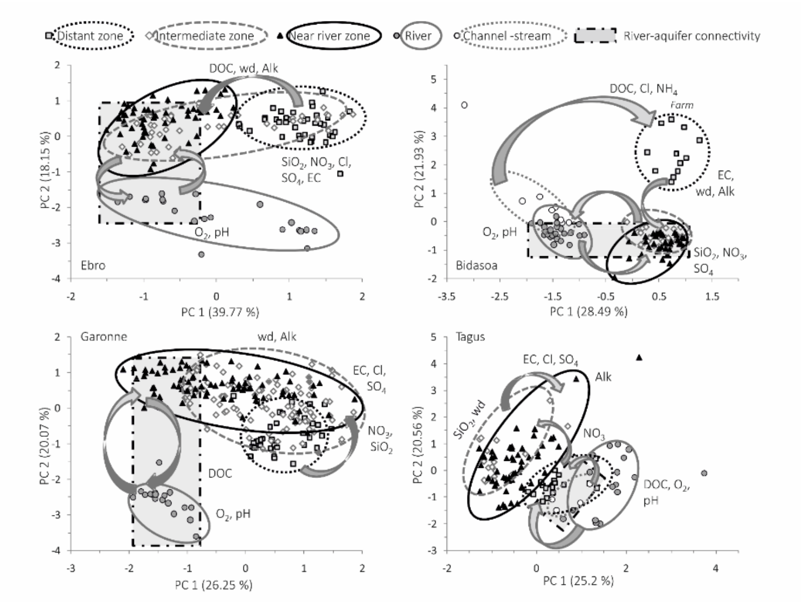

Figure 8: Water characteristics spatial evolution according to water groups location in the I-II factorial plane of the Principal Component Analysis performed in each site. Connectivity is also marked.

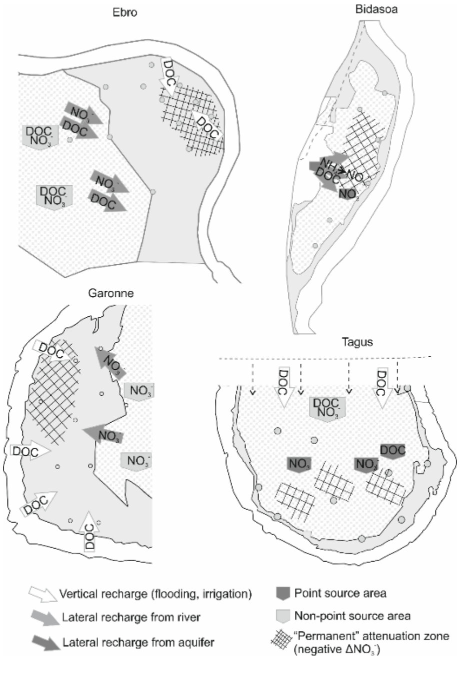

Figure 9: Main sources of N and C in the study sites. Permanent attenuation places (negative ΔNO_3^-) along the year according to the applied approach results (theoretical NO_3^- after EMMA and comparison with observed NO_3^-). See figure 1 for information about land use.