Hydrogeochemistry approach to the identification of flow components under the descending limb conditions of a hydrograph (Corbeira stream, Spain)

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ARTICLE INFO

ABSTRACT

This paper presents a method based on hydrogeochemical signatures for the identification of flow components, from the descending limb to the baseflow, without the direct support of hydrographs. The proposed model was built using chemical analysis of waters from a small agro-forestry catchment having a temperate climate. The sampling was performed every 15 days at the Corbeira stream outlet, from 2004 to 2008. A statistical approach was used with particulate P/dissolved P (PP/DP) values, resulting in a global histogram, within which mini-Gaussian distributions were highlighted. The mean of each group of highlighted PP/DP values, as well as all other selected analytical parameters, were calculated and plotted in Cartesian diagrams. The results showed the hydrogeochemical signatures of the Corbeira stream in the descending limb to baseflow conditions. Scatterplots of the migration of particulate matter showed linear regressions forming $\alpha \neq 0$ to the X-axis, while dissolved compounds showed parallel linearity ($\alpha = 0$) in relation to the same axis. Deflections in the linear behavior point to significant changes in the chemical concentrations from different types of aqueous inputs. Flow components in the descending limb show distinct ranges along the X-axis: the mean PP/DP values. The ranges varying from 3.3 to 2.0 correspond to its upper phases from 2.0 to 0.9 suggests mixtures between inflows and from 0.9 to 0.3 denote subsurface flow dominance. Finally, PP/DP < 0.3 indicates exclusive baseflow conditions. These intervals are specific to the Corbeira catchment as a consequence of its geographical characteristics and should be numerically different from the proposed method if applied to other catchments. However, this method remains valid for application in other small catchments as the PP/DP ranges in the descending limb are defined by the relative behavior between the linear correlations from the hydrogeochemical concentrations plotted in a Cartesian diagram.

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1. Introduction

The chemical composition of river water is influenced by environmental factors interconnected with climate, vegetation, topographic slope, the rock types and soils, hydrogeological cycle, and finally, anthropogenic changes in the catchment area. These processes are highly dynamic on a spatial and temporal scale (Ohrui and Mitchell, 1998; Kalbitz et al., 2000; Holloway and Dahlgren, 2001; Osorio et al., 2003; Pekka et al., 2004).

Perennial rivers are maintained by their baseflow (Freeze, 1972). However, the level of baseflow may fluctuate depending on the recharge caused by rainfall events (Gore, 2006), where the components of surface and subsurface flow exert distinct influences on full flow. Several methods have been proposed since the late 1960s to separate the components of a hydrograph, with the aim of distinguishing flows generated by rainfall events from those found in previous events (Pinder and Jones, 1969; Sklash and Farvorden, 1979; Caissie et al., 1996; Hinton et al., 1997; Soulsby et al., 1998; Ladouche et al., 2001; Schwartz, 2007; Gonzáles et al., 2009).

Much of the environmental monitoring of river systems that occurs worldwide is conducted through regular annual sampling, but without the assistance of hydrographs. In this case, how would it possible to discriminate the influences of overland flow from baseflow in a given period of time? The importance of identifying flow components is important for supporting environmental assessments of rivers in small catchments, as well as characterizing natural and anthropogenic sources and the biogeochemical behavior of compounds in a river system.

The river consists of various sources of water inflow, each with its own physicochemical properties and inherent biogeochemical processes that occur along its course. The identification of flow components becomes possible through the definition of geochemical

signatures of each inflow to the river. The main goal of this study is to propose an identification of flow components from a total river course without the knowledge of hydrographs, based only on hydrogeochemical relationships, especially baseflow predominance. The diagnostic elements have been measured using analytical data from water sampling performed every 15 days on a site near the confluence of the Corbeira stream with the Mero River, Galicia, Spain (Fig. 1), throughout 2004–2008.

2. Study area

The Corbeira stream is a small tributary on the right bank of the Mero River (Fig. 1) that drains forest and agricultural lands, having slopes of between 13% and 25% and ranging from 200 to 400 m in height. Flowing through a mountainous relief, the substratum of the stream is formed essentially of pebble lithoclasts, coarse sands and a lithic bottom. No thick soils are observed near the stream margins. However, inputs of fine particles from tributary fluxes reaching the Corbeira stream outlet tend to be hydrodynamically evacuated over the same storm.

The Corbeira catchment occupies 16.35 km^2 located approximately 30 km SW of A Coruña and bounded by the coordinates 43°11′–13′N and 8°12′–17′W. One-third (33.39%) of this area is used as pastures and for producing crops (5.46 km^2), while the remaining 10.89 km^2 is predominantly covered by forests. The climate is temperate and humid, characterized by an average minimum temperature of 8.4 °C during the winter and an average maximum temperature of 18.6 °C in the summer. The average annual rainfall is 1024 mm/a (1985–2005), with a marked dry period of 2 months during the summer.

The catchment is included in the "Ordenes Complex", a geologic unit composed mainly of schists and granites. In this area, rocks are mainly composed of chlorite schists with dips of approximately 60–70° and a sharp fissure system. This structural context allows the infiltration of water into this lithology and even the presence of springs, where the topography truncates the saturated fissure system. Under the same climatic conditions, the soils of the study area have little variability as a result of the similar mineralogical composition of the regional rocks. Acid umbrisols and cambisols with loamy texture are the dominant pedogenic types (Nachtergaele et al., 2000). The flow that resurfaces in the Corbeira catchment is the shallow subsurface flow from the interfaces of saturated soil or from the bedrock of unconfined aquifers.

The sampling site, located near the confluence of the Corbeira stream with the Mero River, was chosen because it receives all the dissolved and particulate fractions coming from the headwaters. In the vicinity of the sampling site, 65.4% of the area is covered by forest while 25.8% is pasture and 4.0% is used for farming. The remaining 4.8% is impermeable soil which includes buildings and roads.

3. Sampling and analytical methods

Water samples were taken at the site near the confluence of the Corbeira stream with the Mero River from December 2003 to December 2008. Apart from a few exceptions, most samples were collected on dry days, however, some were collected on days with rainfall, mainly in winter and autumn.

The diagnostic elements were determined on water samples collected more or less every 15 days. Each sample was stored in polyethylene bottles, previously washed with 8% HNO$_3$ and then rinsed with deionized water. The samples were preserved at 4 °C to prevent any chemical change during the time between sampling and chemical analysis. Samples were filtered at 0.45 μm. Salinity (Sal) and pH were determined in unfiltered samples using a Crison CM 35 conductivity meter and a Crison 2000 pH meter, respectively. Suspended solids (SS) were determined by gravimetry by weighing the fraction of particulates retained in a filter dried at 105 °C.

In the filtered water, dissolved organic C (DOC) was determined using a Shimadzu total organic carbon analyzer at 5000 °C. After acidification of the filtrate (0.45 μm) with 1% HNO$_3$, the concentrations of dissolved Al (DAl) and dissolved Fe (DFe) were determined by ICP-MS. Total P (TP) was determined on unfiltered samples after digestion with ammonium persulfate (APHA, 1998), followed by the determination of dissolved P (DP) by colorimetry with ascorbic acid (Murphy and Riley, 1962). Particulate P (PP) was calculated as the difference between TP and DP. Total organic N (N$_K$) was obtained by the Kjeldahl method (APHA, 1998).
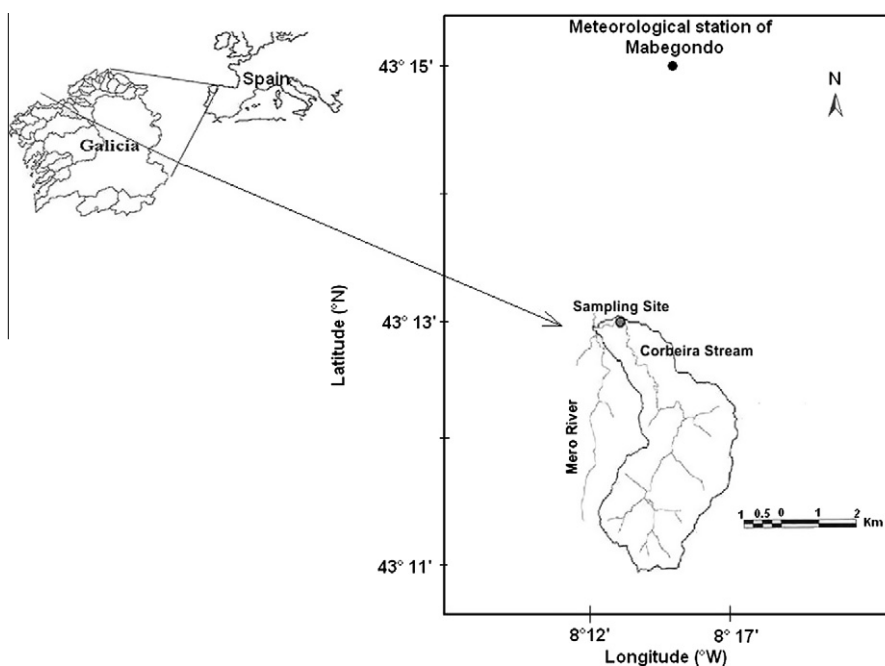

Fig. 1. Location of study area and the sampling station on Corbeira stream, Galicia – Spain.
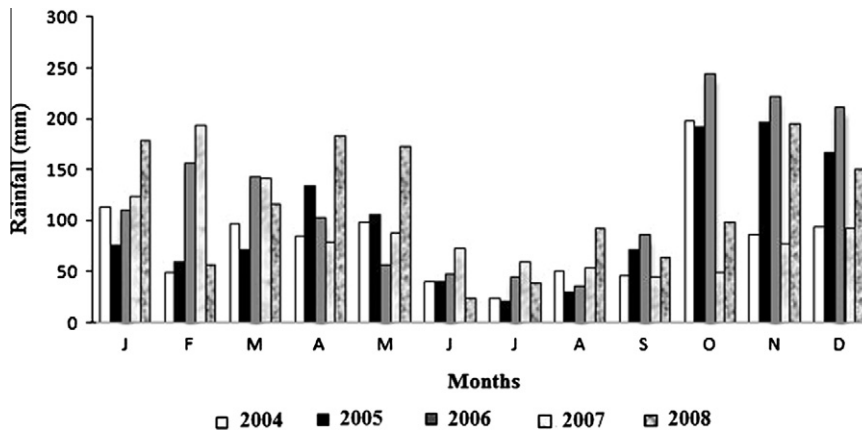
Fig. 2. Monthly rainfall from 2004 to 2008 at the Corbeira catchment (date from the station Mabegondo).

The total precipitation data recorded for each month were obtained from the Mabegondo meteorological station (43°14′50″N, 8°15′47″W), located 4 km from the study area (Fig. 1).

3.1. An alternative method for the identification of flow components in baseflow dominance

The proposed method was conceived following a postulate of Meybeck (1982): "On river transport DOC/POC > 1". In fact, this assumption is contradicted only in the case of strong runoff, when the quantities of suspended solids are exceptionally high. Based on this premise but following an alternative route, the PP/DP ratio for the differentiation of inflows into the Corbeira Stream outlet was adopted for the case study. The DP and PP concentrations were determined, and their respective PP/DP values were calculated, covering the period of this research (2004–2008). A histogram of PP/DP values using a frequency range of 0.25 was constructed (Fig. 3). Within this global histogram, mini-Gaussian distributions were observed and analyzed. Each highlighted group of this sampling established intervals of PP/DP values (Fig. 3, Table 1), mean PP/DP values, and other analytical parameters selected, which were calculated for the purposes of the hydrogeochemical study (Table 1). Considering PP/DP < 0.75, the details of the hydrogeochemical observations allowed the establishment of shorter intervals between the PP/DP values (Table 1), such as from $0 < x \leqslant 0.125$ to $0 < x \leqslant 0.75$, where x is the group PP/DP values.

The calculated values were then plotted in an XY Cartesian scatter diagram, where the X axis = mean values of PP/DP and Y axis = mean values of analytical parameters selected for each interval of PP/DP values (Fig. 4).

4. Results and discussion

Rainfall events provide the means for transport of continental materials to the aquatic ecosystem. Rainfall data (from the Mabegondo meteorological station) over the 4 a were quite variable (Fig. 2): 2004 was a relatively dry year because the rainfall in the months of November and December was below the usual autumn average; both 2005 and 2006 were considered wet; and 2007 was characterized as a very dry atypical year, with scarce rainfall from spring until late autumn; while 2008 was relatively wet, with the highest rainfall recorded during spring. These strong annual variations of rainfall allowed observation of the behavior of the chemical constituents under different seasonal conditions.

The linearity-key expressed by the method applied is related to the basic duality of the conditions that contribute to the river flow: runoff (storm) × baseflow. The first (storm), without doubt, has a strong relationship with the hydrodynamics, and its key variables are SS and PP, regardless of the amount of suspended biomass. Suspended solids are potentially associated with overland flow on forest slopes (Zhang et al., 2007). Thus, for the PP/DP value interval criteria there is a variable attached to hydrodynamics and another
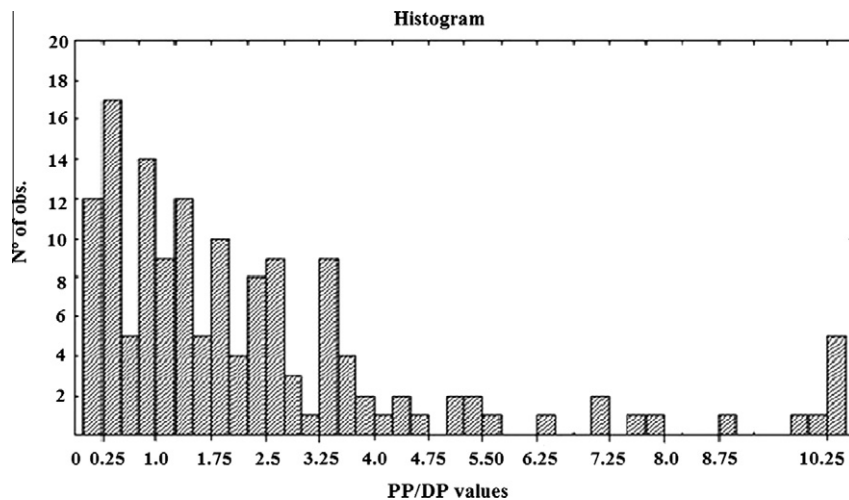

Fig. 3. Histogram of PP/DP values related to the years 2004–2008, Corbeira stream, Galicia – Spain.

Table 1
Mean values of the variables corresponding to the intervals of the PP/DP values related to the group of each highlighted sampling from 2004 to 2008.

Intervals	Mean values									
PP/DP values	PP/DP	PP µg/L	DP µg/L	pH	Sal mg/L	SS mg/L	DOC mg/L	N_K mg/L	DFe µg/L	DAl µg/L
$\{0 < x \leqslant 0.125\}$	0.04	0.35	7.68	7.0	48.3	1.50	1.90	0.08	64.6	10.5
$\{0 < x \leqslant 0.30\}$	0.12	1.24	8.60	7.1	48.0	1.96	1.90	0.28	58.7	9.8
$\{0 < x \leqslant 0.50\}$	0.16	2.40	9.00	7.0	47.7	2.18	1.92	0.30	57.0	9.0
$\{0 < x \leqslant 0.75\}$	0.30	2.72	8.90	7.0	47.5	2.53	1.90	0.27	53.9	8.6
$\{0.5 \leqslant x < 1.25\}$	0.90	8.47	9.71	7.0	47.1	5.30	1.97	0.24	47.0	8.8
$\{1.0 \leqslant x < 1.75\}$	1.35	12.1	9.15	7.0	47.6	6.52	1.88	0.19	42.0	8.76
$\{1.5 \leqslant x < 2.5\}$	2.00	14.1	6.88	6.9	47.9	6.60	2.00	0.28	51.8	11.2
$\{2.5 \leqslant x \leqslant 5.0\}$	3.30	22.8	7.00	7.0	47.2	12.90	2.00	0.24	44.9	13.6
$x > 5$	11.60	52.8	4.19	6.9	48.1	45.60	2.60	0.50	53.2	14.5
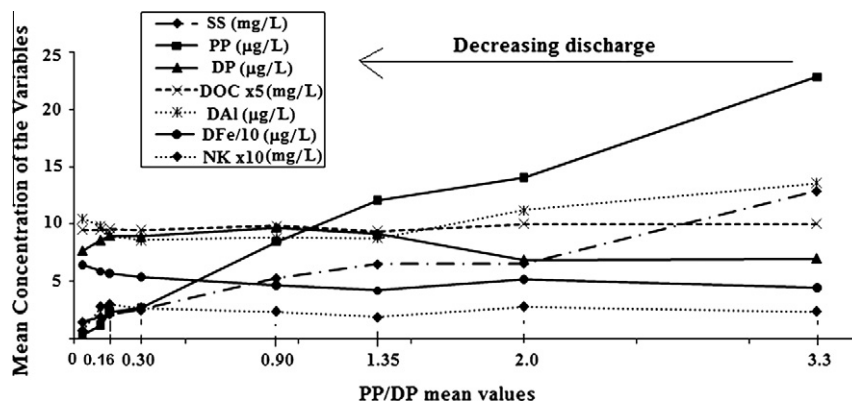
Fig. 4. Geochemical behavior of the variables SS, PP, DP, DOC ($\times5$), DFe (/10), DAl, and N_K ($\times10$), related to the PP/DP mean values.

for dissolved P. Dissolved P is not exclusively linked to overland flow because P-containing compounds may be included in subsurface flows (Driescher and Gelbrecht, 1993; Holman et al., 2008) after crossing soil profiles without being chemically complexed. Therefore, the PP/DP relationship positions a variable that depends almost exclusively on hydrodynamics against another variable that admits several intervening factors, including subsurface inflows and eventual biogenic uptake.

The mean concentrations of SS show first-degree linearity with a strong correlation ($R = 0.98$) in relation to the PP/DP mean values (Fig. 5), and its regression line almost reaches the coordinate's origin (Fig. 5). When the mean of PP/DP reaches minimum values, the same does not occur with SS because, under very low hydrodynamics, some remobilization of finer particles from the bottom stream is still possible. The behavior of mean PP concentrations

is characterized by descending linearity throughout the entire length of the interval $3.3 \geqslant x > 0$ of the mean PP/DP (Fig. 4) within the behavioral expectations for particulate transport in a decreasing discharge regime (Q) in overland runoff. Thus, this linearity corresponds to a first-degree equation ($R = 0.99$; Fig. 6), verifying that their regression line approaches the coordinate axis origin. The scatterplot (Fig. 6) also enable interpretation as a second-degree correlation. However, as demonstrated in a statistical study (Sevon, 1968), considering a strong "R" value (0.99) for a specific first-degree linear correlation, both propositions show little or no improvement (standard error of estimate) over its respective "x" calculated values.

There is a nuance in the range $3.3 \geqslant x > 0$ (Fig. 4) that matches the exclusive baseflow conditions: the observation of a more accentuated fall in the downward trend of the PP mean concentrations,
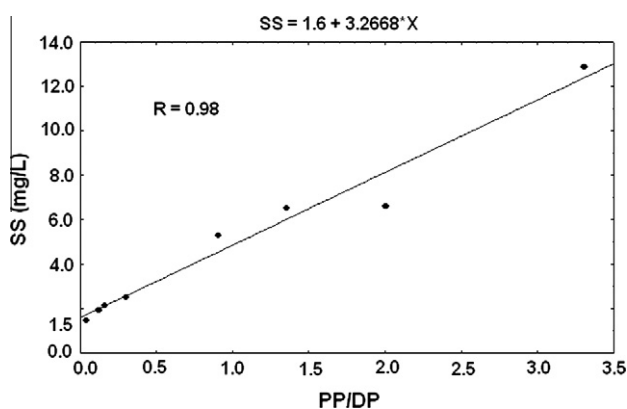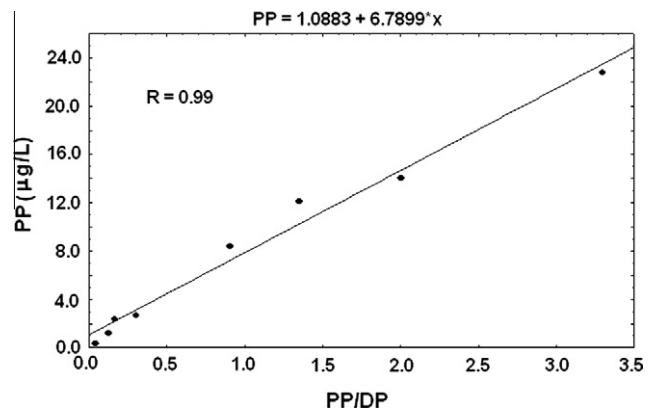

Fig. 5. Linear regression with plots of the SS (mg/L) mean values related to the PP/DP mean values.

Fig. 6. Linear regression with plots of the PP (µg/L) mean values related to the PP/DP mean values.

due to the decrease in primary productivity, is probably due to the limited availability of nutrients at this stage of the hydrograph ($x \leqslant 0.16$).

The DP hydrogeochemical behavior follows the export as a soluble compound or in an ionic state, but the concentrations are subject to influences when submitted to waters of overland flow or subsurface flow. The mean DP concentrations are stable for PP/DP > 2 (Fig. 4), still in predominance of overland flow in the descending limb of the hydrograph. Nevertheless, the PP/DP mean values in the range $2.0 \geqslant x \geqslant 0.3$ show a rising inflection (Fig. 4), resulting from the converging inflows of subsurface water with the stream flow. In this case, the influence of overland flow decreases and the indication is that subsurface waters contain substantial DP concentrations.

Considering that felsic rocks have mean P levels from 0.05% to 0.1% (Turekian and Wedepohol, 1961), its dissolution from soils, even if complete, would give a negligible amount of DP. By the same token, in the schist area of Galicia, Calvo and Macías (1993) indicated a DP standard of 2 µg/L in river flows without anthropogenic influence, obviously suggesting that the DP was of biogenic, natural origin. Considering the standard indicated by Calvo and Macías (1993), the mean DP concentration in this study, running from 4.19 to 9.71 µg/L (Table 1) is conspicuous evidence of contamination by inputs of agricultural effluents in the catchment area.

The magnitude of human intervention in terms of incorporating DP in river flow for a presumable period of over 15 a is denoted by abnormal DP concentrations (2–$4.5 \times$ the regional natural standard). These abnormalities cover the entire range of the mean PP/DP values (Fig. 4) and are not unique to storm peaks. Without the effect of equalization applied to individualized storm peaks, Rodríguez-Blanco et al. (2010) recorded DP values on the order of 50 µg/L. These observations indicate that hydrophilic dissolved organic P and soluble PO_4^{3-} are DP species that infiltrate easily into the subsurface (Kaiser, 2001), and this undoubtedly would be the preferred route for DP export. Taking different approaches, Pommel and Dorioz (1997), in another agricultural catchment, and Rodríguez-Blanco et al. (2010), in this same Corbeira catchment, reached the same conclusions. Considering these observations, the abnormalities of the mean DP levels appear to be primarily a consequence of rainwater infiltration in agricultural lands. This result is the reason why subsurface waters should contain substantive DP concentrations; sufficient to cause the upward inflection of DP linearity in the range $2.0 \geqslant x \geqslant 0.3$ of mean PP/DP values (Fig. 4). Finally, in conditions of exclusive baseflow, especially under warm climatic and prolonged drought conditions, there is a clear decay of DP due to biogenic uptake and the reduction of DP intake from the subsurface waters.

The DAl variable may correspond to micaceous minerals or clay minerals both of colloidal dimensions and even other aluminosilicates of pedogenic origin, transported by flushing as well as to free Al (Al^{3+}) under special circumstances. Aluminous minerals are geologically abundant in rocks of the studied catchment, and the release of Al^{3+} ions is predictable if intensification of weathering occurs. The mean DAl values followed the same decreasing trends of SS and PP values in the range $3.3 \geqslant x \geqslant 1.35$ of the mean values of PP/DP (Fig. 4), preceding the exclusive hydrochemical conditions of the baseflow. This general behavior is also a consequence of a decrease in the Q values. The Al values are mainly linked to colloidal minerals in conditions of baseflow dominance, yet dependent on residual overland flow. However, if there is an increase in the mixtures of sub-surface flow, DAl becomes available only in the ionic form. In the first stage, its values produce the stabilization of decreasing linearity (Fig. 4). Finally, a conspicuous reversal of this linearity occurs under exclusive baseflow conditions (PP/DP < 0.3). This behavior can be attributed to subsurface inflows, where the ionic state is the only significant form of Al inputs.

The behavior of DFe depends on the different forms in which the Fe can be present in nature after its release through hydrolysis from a primary or secondary mineral. For conditions of PP/DP > 2.0, with the definite predominance of overland runoff, DFe may consist essentially of Fe ions and/or dissolved Fe compounds as well as colloidal particles (usually goethite).

The definition of the preferred route for Fe transport was predicted by the contraposition of mean DFe concentrations reported for the PP/DP mean values (Fig. 4), which is implicitly related to the Q changes. The increase in hydrodynamics impart the ability to remove particulates and to transport solutes. The difference is that, considering the decrease of Q, the ability to transport particulates varies granulometrically in terms of the total load transported. In contrast, a decreasing Q, which results in the loss of hydrodynamics (the river gradient assumed to be constant) and a reduction in water volume, does not affect solute concentrations in the aquatic environment when it reaches the constant of equilibrium. Thus, compounds that are either dissolved or in an ionic state and are perfectly homogenized in aquatic transport, basically maintain their concentration and, therefore, exhibit parallel linearity to the abscissa axis (mean PP/DP values).

The behavior of the mean DFe values in contraposition to the mean PP/DP values (Fig. 4) indicates that in the Corbeira catchment, the preferred route for Fe export, in broad descending limb conditions, is in the form of soluble compounds or the ionic state. Finally, the inflexion to higher mean concentrations in exclusive baseflow conditions suggests that their mean concentrations in subsurface flow are higher than in residual overland flow.

The behavior of the mean DOC concentrations is characterized by small variations in their linearity (amplitude of 0.11 mg/L, Table 1) along the intervals of the mean values of PP/DP and showing a parallel disposition to the abscissas axis (Fig. 4). As a soluble compound, DOC is flushed, and the pedogenic concentrations are transported during periods of rainfall. DOC exports in overland runoff, in principle, are influenced by rainfall intensity, being diluted in the respective volumes of flow generated by these events until it reaches its constant of equilibrium. Therefore, DOC linearity during the descending limb shows that this compound rapidly reaches the constant of equilibrium soon after the rainfall event. The mean DOC concentration remained stable, even under conditions of exclusive baseflow. Apparently, at this hydrograph stage, even under dry and warm conditions, DOC uptake was not statistically discernible. Presumably, there is a balance between nutrient availability through the subsurface flow pathway, and biogenic uptake, a feature that has been noted in natural aquatic environments (Paerl, 1974; Farjalla et al., 2006).

The N_K comprises NH_4^+ + dissolved organic N (DON) + particulate organic N (PON), meaning that this parameter has differing geochemical behaviors depending on the degree of participation of its constituents in water flows. The general behavior of mean N_K values shows little variability in its linearity along the intervals $3.3 \leqslant x \leqslant 0.3$ of the mean PP/DP values (Fig. 4). The variation of their mean concentrations barely reaches 0.3 mg/L (Table 1). The baseflow is dominated by DON and NH_4^+, as a result of the solubilization and mineralization of organic matter (OM). In fact, the flow of total N in forest soils has been reported as dominated by DON (Lepisto et al., 1995; Currie et al., 1996). Even so, increases in the hydrodynamics can expand the transport of particulate and soluble N_K. Inversely, a decrease of Q, considering these different forms of N export, does not affect the average concentrations of the dissolved fractions but gradually decreases those of the particulate fractions. Finally, in conditions of exclusive baseflow and in prolonged dry and warm weather, it is possible to register a clear N_K depletion (NH_4^+) produced by the biogenic autotrophic uptake and reduction of N_K intake from subsurface waters.
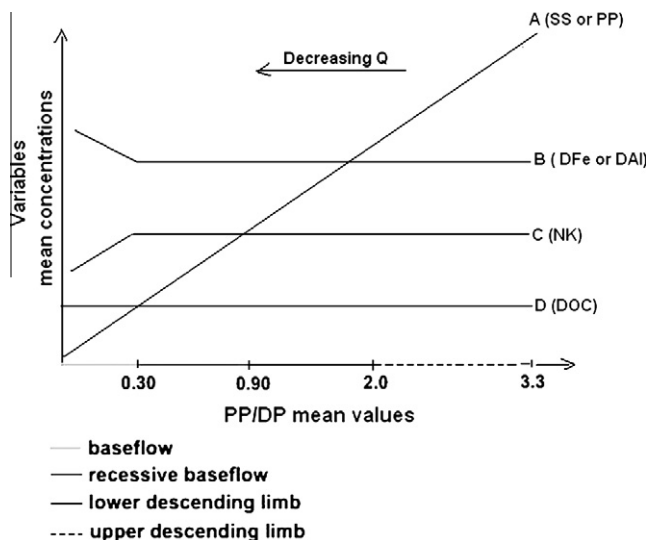
Fig. 7. Schematic diagram of the Cartesian morphology of chemical compounds transported in stream water as particulate (A) and dissolved (B, C, and D) forms, in descending limb conditions of the hydrograph.

4.1. Hydrogeochemical signatures related to the hydrographic components in a descending limb

The transport of particulates is clearly dependent on the hydrodynamics. The plot of the mean values of their respective parameters in the Cartesian diagram, in relation to the intervals of mean PP/DP values, showed a first-degree linearity and angles $\alpha \neq 0$ in relation to the abscissa axis (Fig. 7). The regression lines of the particulates nearly reach the intersection of the coordinate axis. The decreasing discharge and gradual increase of subsurface flow resulted in a decrease of the linearity representing the particulate fraction due to the compositional differences that characterize the water inflows of overland flow versus subsurface flow. This condition occurs from the descending limb toward the domain of the recession baseflow of a hydrograph.

In descending limb conditions in the hydrograph, the migration of compounds, whether, dissolved or in an ionic state, is essentially dependent on the infiltration of subsurface waters from the soil and through the lithogenic environment, taking a substantially longer time than that observed in the overland flow. These subsurface waters contain products of mineral hydrolysis and OM biodegradation in soils. The plot of the mean values of the analytical parameters exported in this way, in contraposition to the intervals of the mean PP/DP values, also exhibited first-degree linearity but with parallel provisions in relation to the abscissa axis ($\alpha = 0$) (Fig. 7). This feature can suffer statistically discernible deflections in exclusive baseflow conditions under prolonged drought: descendant by biogenic uptake and the decrease of nutrient intake and ascendant by the inputs of hydrolyzed products from the subsurface waters.

5. Conclusions

The contraposition of the mean values of the hydrogeochemical variables studied in relation to the intervals of mean PP/DP values allowed establishing the evolutionary conditions along the descending limb of a hydrograph. In the case of the Corbeira stream, the mean PP/DP value interval of $3.3 \geqslant x \geqslant 2.0$ represents the early stages of the descending limb with the predominance of residual overland flow. In the interval $2.0 > x \geqslant 0.9$, mixture between the surface and subsurface inflow occurs which is typical of the final stages of the descending limb. In the $0.9 > x \geqslant 0.3$ interval the

predominance of the influence of subsurface waters is observed (recession baseflow). Finally, the exclusive baseflow is characterized by PP/DP < 0.3 mean values. These observed PP/DP intervals are specific to the Corbeira catchment as a consequence of its geographical characteristics, including surface occupation, drainage gradients, climatic regime and nature of soils. The same intervals should be numerically different when applying the proposed method in other cases. However, this method remains valid for application in other small catchments, as PP/DP ranges are defined by the relative behavior between linear correlations referring to hydrogeochemical concentrations when plotted in Cartesian diagram. Therefore, a baseflow stage will have its interval limited by the projection of the principal inflexion point of the linear correlation of N_K and/or DAl over the X-axis. The intersection (equally projected over the X-axis) between the linear regressions of PP and N_K will mark the beginning of the recessive baseflow stage.

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