Dissolved solids and suspended sediment dynamics from five small agricultural watersheds in Navarre, Spain: A 10-year study

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ABSTRACT

Dissolved solid (DS) and suspended sediment (SS) loads are considered relevant environmental problems. They are related to a wide range of on-site and off-site impacts, such as soil erosion or salinization of water bodies. In this study, the dynamics of DS and SS concentrations and loads were assessed in five small watersheds covering representative agricultural land uses in Navarre (Spain). To this end, discharge, DS and SS concentration data were collected during ten hydrological years at each watershed outlet, and loads were computed from discharge and concentration values. DS concentration followed a seasonal pattern imposed by the availability of water, with higher concentrations recorded in low-flow periods and lower concentration in the high-flow period. SS concentration was extremely variable, with a range of 2 - 4 orders of magnitude in concentration for any specific discharge. Temporal variations (both intra- and inter-annual) in DS loads were explained by differences in runoff, whereas those of SS were not, being the SS loads associated mainly with specific high flow events. These temporal patterns were observed for both agricultural (this study) and non-agricultural (literature) watersheds. From the data in the Navarrese watersheds and those available in the literature, we inferred that agricultural land use, in general, tends to increase the concentration of both DS and SS. Regarding DS and SS yields, the effects of agricultural land use on DS yields are controlled by the changes in runoff rather than the (small) changes in DS concentration. In this sense, land uses changes expected to increase runoff (i.e., a shift from forested to arable or from rainfed to irrigated agriculture) would increase DS yields. On the other hand, agricultural land use tends to increase SS yields, although the effect is highly variable depending on site-specific factors, both natural (e.g., watershed shape) and anthropogenic (e.g., degree of soil conservation practices). In the Navarrese watersheds, DS yields ranged from 1.1 to 2.2 Mg ha^{-1} year^{-1} whereas SS yields ranged from 0.3 to 4.3 Mg ha^{-1} year^{-1}. DS yields seem to dominate under non-agricultural conditions and in most agricultural land uses at the small watershed scale. On the other hand, SS yields dominate in watersheds with increased soil erosion as a consequence of arable land use over erosion-prone watersheds.

Keywords: hydrology; solute dynamics; sediment dynamics; flux of solutes; flux of suspended matter; land use.

1. Introduction

Soil erosion and associated sediment loads is regarded as one of the main environmental problems. In many cases, the fine soil fraction is more easily eroded and richer in organic matter and nutrients (Brady and Weil, 2012). Due to this loss of fertility, severely eroded fields require a major addition of synthetic fertilisers if production levels need to be maintained (Merrington et al., 2002). Off-site suspended sediment has several impacts in water courses: physical (siltation of reservoirs, higher costs of drinking water treatment, etc.), chemical (desorption of nutrients, heavy metals, etc.) and biological (affection to fishes, invertebrates, macrophytes, etc.). Although soil erosion rates vary widely in any specific set of conditions, cultivated land tends to produce, in general, higher erosion rates (Montgomery, 2007; Cerdan et al., 2010;_García-Ruiz et al., 2015). As a consequence, significant amount of suspended sediment will be exported through the watershed outlet in cultivated areas.

Dissolved loads contribute to the salinization of downstream water bodies, which can affect its suitability for water consumption or impair its ecosystem value (Nielsen et al., 2003). The solutes delivered to streams depend mainly on lithology and the duration of water circulation, and they are supplied by tributaries as well as surface runoff, interflow and groundwater flow (Swiechowicz, 2002). However, several anthropogenic factors may contribute to the stream soluble load. For instance, de-icing road salts is a significant source of chloride and sodium (e.g., Godwin et al., 2003) and wastewater effluents supply considerable amounts of a wide range of soluble constituents such as chloride, sulphate, sodium, phosphate, etc. In addition, both cultivated land and pastures may contribute to streams salt loads (e.g., Anning and Flynn, 2014).

The role and interactions of suspended and dissolved loads in streamflow has been extensively studied in watersheds. For instance, Grove et al. (1972) studied the dissolved and solid loads by some West African rivers; Subramanian (1979) studied it in Indian rivers; Lewis and Saunders (1989) in the Orinoco River; and Gaillardet et al. (1997) in the Amazon River. These studies (along with others available in the literature) were conducted in regional watersheds (from 10^3 to 10^6 km^2), they are relatively short termed and present low frequency in data acquisition (e.g., following a biweekly to monthly sampling schemes during one or up to a few years). More recent studies such as those by Négrel et al. (2007) in the Ebro River (Spain) or Ollivier et al. (2010) in the Rhone River (France) partially overcome this weakness with a long-term study (Ebro) or a higher sampling frequency (Rhone). However, in such extensive watersheds, it can be hard to relate observed hydrological behaviour to specific controlling factors such as climate, geology or land use.

In contrast to large regional watersheds, suspended and dissolved loads in small watershed (<10 km^2) have been studied to a lesser extent. In fact, for the suspended sediment specifically, in a compilation of suspended sediment yields in Europe, Vanmaercke et al. (2011) recognized the lack of available data for small watersheds. Among those studies conducted at the small watershed scale in Spain, Llorens et al. (1997) studied particulate and soluble mass transfer in a mountainous 0.4 km^2 watershed in which terraced-cultivation had been abandoned. Lasanta et al. (2001) studied a 6.5 km^2 flood irrigated watershed. Outeiro et al. (2010) estimated the contribution of suspended or dissolved loads in relation to specific high-flow events (floods) events in a watershed covered by forest and cultivated fields. Durán-Zuaso et al. (2012) studied a 6.5 km^2 watershed with mixed land use. Also, Nadal-Romero et al. (2012) reported the proportion of suspended and dissolved loads for four small watersheds in the Pyrenees.

From an operational point of view, small watersheds allow for some degree of homogeneity in climate, geology and land use; have minor or no flood plains; and only local contribution of groundwater flow (Buttle, 1998). Therefore, they may seem to be better suited to understand the specific processes generating the suspended and dissolved loads in streamflow. Despite this advantage, results are not easily extrapolated to larger watersheds due to the scale dependency of many hydrological processes, in particular suspended sediment and dissolved solids dynamics (De Vente et al., 2007; Tiwari et al., 2017). As it was the case in large watersheds, most of the available studies are generally short termed, covering from a few flood events (Outeiro et al., 2010) up to three hydrological years (Durán-Zuaso et al., 2012; Gao et al., 2014). Therefore, these studies may have low representativeness given the short study period. In fact, the episodic nature of suspended sediment delivery requires long-data set for an adequate estimation (e.g., O’Brien et al., 2016). In addition, most of those studies were located in non-agricultural watersheds. In fact, to the best of our knowledge, only a few studies have specifically analysed the dynamics of suspended sediment and dissolved solids in agricultural watersheds (Carling, 1983; Hubbard et al., 1990; Lasanta et al., 2001; Outeiro et al., 2010).

In Navarre (northeast Spain), the consequences of agriculture on soil erosion and water quality are investigated in a network of experimental watersheds implemented by the former *Department of Agriculture, Livestock and Food* of the Government of Navarre. Four watersheds covering representative land uses in the region are included in this network. Agricultural management in these watersheds is the typical for the different land uses in the region, since the objective of the network is to adequately characterize the behaviour of these watersheds under standard management conditions. Previous works have described the physical and agronomic characteristics of each watershed, along with the quality of the water generated in terms of suspended sediment, nitrate or phosphate (Casalí et al., 2008, 2010; Merchán et al., 2018). In addition, other studies have been performed in these watershed. For instance, Giménez et al. (2012) analysed the factors controlling sediment export whereas Chahor et al. (2014) calibrated and validated a model (AnnAGNPS) of sediment yield in one of the watersheds. However, to the date no data have been presented on the different dynamics of the dissolved solids and the suspended sediment in these watersheds.

In this context, the main objectives of this study were (i) to assess the dynamics of dissolved solids and suspended sediment concentration and loads in small watersheds in Navarre in which the agricultural land use is dominant; (ii) to estimate a long-term (10 years) average suspended and dissolved yield in each of these watersheds; and (iii) to gain insight in the controlling factors underpinning these processes through comparisons among watersheds and with information available in the literature.

2. Methods

2.1. Experimental watersheds

The network of experimental agricultural watersheds (Government of Navarre, 2018a) is depicted in Fig. 1 and relevant data is presented in Table 1. The watersheds are located in headwaters areas, do not have significant flood plains or groundwater inputs, and present uniform climate over the watershed area. Therefore, they can be considered "small" watersheds (10^{-2} to 10^{2} km^2) according to the operational definition of Buttle (1998). A detailed description of the experimental watersheds, its agricultural management and hydrological behaviour is available elsewhere (Casalí et al., 2008, 2010; Merchán et al., 2018). A summary with the information considered of relevance in this study is provided in this section.

La Tejería watershed covers an area of 169 ha and is located in the central western part of Navarre (Casalí et al., 2008). Its climate is humid sub-Mediterranean, with average annual precipitation of 755 mm and average annual temperature of 12.3 ºC. Slopes are homogenous with an average value of 15%. The prevailing soil class is Vertic Haploxerept (Soil Survey Staff, 2014) located on eroded hillslopes and soil organic matter content ranges between 1.5% and 2.5%. These soils are relatively shallow (0.5–1.0 m deep) with silty clay texture. The watershed is almost completely (93%) cultivated with winter grain (mainly wheat and barley). Tillage is conventional and frequently parallel to the contour lines. Other management practices such as planting dates or fertilization rates are the typical of the area (Casalí et al., 2008).

Latxaga watershed covers an area of 207 ha and is located in the central eastern part of Navarre (Casalí et al., 2008). Its climate is humid sub-Mediterranean, with an average annual precipitation of 861 mm and average annual temperature of 11.8 ºC. The prevailing soil classes are (para)Lithic Xerorthent and Fluventic Haploxerept (Soil Survey Staff, 2014), both with silty clay loam texture. The first soil class is shallow (< 0.5 m deep), whereas the second is deeper (> 1 m) and located on swales and hillslopes where eroded soil accumulates. Average slope is 19% and soil organic matter content ranges between 1.0% and 3.8%. Land use, crop productivity and soil management practices are similar to those described for La Tejería watershed (Casalí et al., 2008), although the proportion of non-arable surface (such as riparian areas) is higher than that in La Tejería, with an arable land proportion of 89% of the watershed surface.

Oskotz Principal watershed comprises 1688 ha in the north part of Navarre (Casalí et al., 2010). Its climate is sub-Atlantic, with an average annual precipitation of 1278 mm and average annual temperature 10.6 ºC. The slope in the hillsides are in the range of 10–65% but only around 5% in the valley bottom. The prevailing soil class is (para)Lithic Ustorthent and (Soil Survey Staff, 2014), with 1 m depth and clay loam texture, located in the eroded hillslope. Soil organic matter content ranges between 2.5% and 6.4%. Most of the watershed is covered with forest (61%), mainly *Fagus sylvatica*, *Quercus pyrenaica* and *Pinus spp*., whereas the remaining area is covered by pastures (23%) for cattle-breeding and arable land (13%). Within the Oskotz watershed, a 434 ha sub-watershed almost fully covered with forest (83%, namely Oskotz Forested) is also monitored. The forests are cleared for wood production with a frequency of 6-8 years (Casalí et al., 2010).

Landazuria watershed covers an area of 480 ha and is located in southern Navarre (Merchán et al., 2018). Its climate is dry Mediterranean, with an average annual precipitation of 417 mm and average annual temperature of 13.2 ºC. The watershed is relatively flat, with slopes between 3% and 5%. Typic Haplustepts and Typic Calciustolls (Soil Survey Staff, 2014) are the most common soil classes in the watershed with clay loam or silt loam textures and shallow depth. Soil organic matter contents range between 1.7% and 2.7%. Over 88% of the watershed area is cultivated, with about 60% of the total cultivated area under pressurized irrigation systems. The rest of the cultivated surface is rainfed agriculture. Barley is the main rainfed crop while maize, winter cereal, tomatoes and onions are the main crops in the irrigated areas (Merchán et al., 2018).

The Navarrese network of watersheds covers eminently agricultural watersheds. There is a gradient in use intensity from intensively used and managed arable land (irrigated), two typical rainfed arable land, and finally a watershed with mixed forest and pastures land use (with a forested sub-watershed). We use data mainly from our forested watershed (and that available in the literature) to gain some insight of the analysed processes in non-agricultural watersheds.

2.2. Meteorological data

Each watershed has an associated meteorological station. In La Tejería, Latxaga and Oskotz, the station is located within the watershed, whereas in Landazuria it is located 5 km to the south (Government of Navarre, 2018b). The stations associated with the experimental watersheds are: Villanueva de Yerri (La Tejería), Beortegi (Latxaga), Oskotz (Oskotz) and Bardenas-El Yugo (Landazuria).

2.3. Hydrological stations

The former *Department of Agriculture, Livestock and Food* of the Government of Navarre installed a hydrological station at each watershed outlet. The installation year and the available information for each watershed are presented in Table 1. Water level is recorded at 10 minutes intervals. The discharge measurement device consisted of a V-notch weir in three of the watersheds (La Tejería, Latxaga and Oskotz, with two stations in this last watershed) and an H-type flume in the remaining one (Landazuria).

Discharge was calculated from water level data, which were monitored using electronic limnigraphs and data loggers. Water discharge was also directly measured for verification using a propeller-type current meter and triangular and rectangular sharp-crested weirs, covering a wide range of water levels. All measurement methods yielded consistent results.

2.4. Water quality sampling and analysis

At each watershed, water samples were taken every 6 hours (3, 9, 15 and 21 hours, solar time) from a hemispheric hollow, 0.66 m in diameter, made in the downstream face of the weir. For this purpose, an automatic programmable sampler was used, consisting of 24 bottles (500 mL). The four samples collected each day were mixed together prior to analysis to provide a representative daily average sample for determining suspended sediment and dissolved solids concentrations. Water samples were analysed following the standard methods for water quality parameters at the Agricultural Laboratory of the Department of Agriculture and Food of the Government of Navarre. Suspended sediment concentration (SS) and major dissolved constituents (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^- CO_3^{2-}, NO_3^-) were determined in each composite sample. Cations were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES; PerkinElmer DV-2000, Waltham, Massachusetts, U.S.); Cl^-, SO_4^{2-} and NO_3^- by ionic chromatography technique (HPLC; Thermo Fischer Scientific Dionex DX-120, Bremen, Germany); HCO_3^- and CO_3^{2-} by acid-base volumetric technique; and suspended sediment by gravimetric technique (0.7 µm filter pore size). The charge balance ($100\cdot[\Sigma$ cations – Σ anions]/[Σ cations + Σ anions]) of the samples was determined and found to be within ±10 % for more than 97% of the samples, suggesting that all relevant constituents were considered in the analysis. Dissolved solids concentration (DS) was then computed by addition of the individual dissolved constituents.

Several issues produced missing samples for specific days (e.g., equipment malfunctioning, not enough flow for sample collection, etc.). In addition, not every constituent could be measured in every single sample (for instance, when the automatic sampler did not collected enough water).

Since October 2012, the analytical determinations were limited to anions and nutrients. Therefore, a multi-linear regression was obtained from the period in which all major constituents were determined. Samples utilized for each regression, coefficient of determination (R^2) and equations obtained are presented in Table 2.

After preliminary screening of the available database, the period from October 2006 to September 2016 (hydrological years 2007-2016) was selected for this study. This period presented: (1) a complete meteorological record, with only a few days of sensor failures (12 days in Oskotz and 4 days in La Tejería, <0.4% and <0.1% of the ten-year study period, respectively); (2) a continuous water level record, with only minor (in the order of several hours) failures in the recording equipment (<0.05% of the study period); (3) the most complete water quality data set. In fact, 69% of the days were sampled in La Tejería, 66% in Latxaga, 87% in Oskotz Principal, and 83% in both Oskotz Forested and Landazuria. The lower values of La Tejería and Latxaga are related with the fact that these watershed dry up (non-measurable discharge) for significant periods in summer, especially those of dry years. Even in the driest year of this study period, 157 and 155 samples were collected in La Tejería and Latxaga, respectively. In addition, there was no previous data for Landazuria (the monitoring of this watershed began in the summer of 2006) and there were several years with major failure equipment for the different watersheds in the previous years. For instance, no sample was collected in Oskotz Principal in the hydrological year 2003 and only 22 samples were collected in La Tejería in 2006. In this way, we ensured a relatively consistent data availability for the different watersheds and a similar study period, making comparisons between watersheds more reliable.

2.5. Loads computation

Daily average discharge data was used in combination with daily SS and DS measured concentrations to compute daily suspended sediment loads and daily dissolved solids loads. In order to obtain load estimation for the whole study period, three different approaches were used (Meals et al., 2013). The methods used were:

a) Numeric integration: it is based on the integration of the daily load. For those days in which there was no load available, the monthly median concentration of the sampled period was assigned to the volume of water measured in non-sampled days.

   - $Load_{07-16} = \sum_{i=1}^{n} c_i q_i t_i$ Eq. 1

     Where c, q and t are the concentration, discharge and duration of the i^{th} time interval respectively, and $Load_{07-16}$ is the load for the whole study period (hydrological years 2007-2016).

b) Regression: a rating curve was fitted to the observed data and used to estimate the load for the selected study period. Daily loads were estimated based on the relationship of observed loads with discharge, time and season. This estimation was performed using the US Geological Survey software LOADEST (Runkel et al., 2008).

   - $Log(Load) = a_0 + a_1 Log(Q) + a_2 Log(Q^2) + a_3 sin(2\pi\ dtime) + \mathrm{a}_4 \cos(2\pi\ dtime) + a_5 dtime + a_6 dtime^2$ Eq. 2

     Where *Load* and Q are the daily load and the daily average discharge, $a_0 \dots a_6$ are the seven parameters of the rating curve and *dtime* is decimal time.

c) Ratio estimator: this method assume that the flow weighted concentration in the period with available data is representative of that of the complete study period. Therefore, the ratio of complete flow over sampled flow is used to correct the observed load. Some corrections are then applied according to the covariance of loads and flow. In particular, the Beale ratio (Richards et al., 2007) was used:

- $Load_{07-16} = Load_{obs} \left[\frac{Q_{07-16}}{Q_{obs}}\right] BCT$ Eq. 3

  Where $Load_{obs}$ and Q_{obs} are respectively the total load and discharge of those days that were sampled, while $Q_{07\text{-}16}$ is the discharge for the whole study period and *BCT* is a bias correction term.

After load computation, annual yields were obtained by dividing the annual loads by the watershed surface.

3. Results

The structure of this section is as follows: the general results regarding precipitation and discharge in the watersheds are briefly described in order to provide the hydrological context of the study period (section 3.1); then, the dynamics in the concentration (section 3.2) and exported loads (section 3.3) of SS and DS are described; finally, section 3.4 present the long-term yield estimation for the analysed watersheds.

3.1. Precipitation and discharge

During the hydrological years 2007-2016, annual average precipitation ranged between 423 ± 80 mm (average ± standard deviation) in Landazuria and 1391 ± 326 mm in Oskotz, with intermediate values in La Tejería and Latxaga (793 ± 216 mm and 950 ±

285 mm, respectively) (Table 3). The hydrological year 2013 was the wettest for all the watersheds, with precipitation more than two standard deviations higher than the average (Table 3). The driest hydrological year differed among watersheds, being 2010 for Oskotz, 2011 for Latxaga and 2012 for La Tejería and Landazuria. In addition, the year 2012 was the second driest year in Oskotz and Latxaga.

For the same period, water yield in La Tejería ranged from 4 to 415 mm (222 ± 126 mm), with an average runoff coefficient of 28%; in Latxaga it ranged from 38 to 513 mm (250 ± 129 mm), runoff coefficient of 26%; in Oskotz Principal water yield ranged from 349 to 1161 mm (639 ± 238 mm), runoff coefficient of 46%; in Oskotz Forested it ranged from 353 to 1275 mm (646 ± 265 mm), runoff coefficient of 46%; and finally in Landazuria water yield ranged from 42 to 143 mm (98 ± 30 mm), with a runoff coefficient of 23%. Note that irrigation is not considered for the computation of runoff coefficient in this last watershed.

3.2. Dynamics in dissolved solids and suspended sediment concentration

The observed dynamics in the behaviour of DS and SS concentration were significantly different. Daily discharge along with DS and SS daily concentrations are presented in Fig. 2 and 3 for the different watersheds. Selected statistics for each watershed are presented in Table 4. The degree of variation in DS concentration in the different watersheds (Fig. 2) was relatively low. In contrast, SS concentration was extremely variable (note the logarithmic scale in Fig. 3). In the case of DS concentration, average and median values were relatively similar (± 2%, Table 4), and the coefficient of variation (CV) was low, ranging from 13 to 20% in the different watersheds. Average and median SS concentrations differed significantly being the average concentration between 3.5

and 5.8 times higher than median for the different watersheds (Table 4). In fact, the CV of SS concentration ranged from 220 to over 750%.

Regarding the specific values obtained (Table 4), DS concentrations were the highest in Landazuria (median: 2275 mg L^{-1}; inter-quartile range (IQR): 1960 to 2547 mg L^{-1}), followed by La Tejería (median: 547 mg L^{-1}; IQR: 494 to 612 mg L^{-1}), Latxaga (median: 482 mg L^{-1}; IQR: 440 to 529 mg L^{-1}), Oskotz Principal (median: 420 mg L^{-1}; IQR: 376 to 475 mg L^{-1}) and Oskotz Forested (median: 327 mg L^{-1}; IQR: 300 to 355 mg L^{-1}). Median DS concentration in each watershed was significantly different (Wilcoxon-Mann-Whitney Rank-Sum Test, $p<0.001$; Helsel and Hirsch, 2002) than that in any other watershed. In the case of SS concentrations (Table 4), the highest values were recorded in La Tejería (median: 0.18 g L^{-1}; IQR: 0.04 to 1.08 g L^{-1}), followed by Latxaga (median: 0.04 g L^{-1}; IQR: 0.02 to 0.10 g L^{-1}), Landazuria (median: 0.02 g L^{-1}; IQR: 0.01 to 0.05 g L^{-1}) and both watersheds at Oskotz (median: 0.01 g L^{-1}; IQR: 0.00 to 0.03 g L^{-1}). Median SS concentration in each watershed was significantly different than that in any other watershed (Wilcoxon-Mann-Whitney Rank-Sum Test, $p<0.001$; Helsel and Hirsch, 2002), with the exception of both watersheds at Oskotz, with no significant differences between them ($p>0.05$).

DS concentration presented a characteristic seasonal pattern in every watershed. In the non-irrigated watersheds (namely La Tejería, Latxaga and both stations in Oskotz), the highest DS concentrations were observed at the end of the summer, late September to early November (Fig. 2). This pattern was detected even in those summers where sampling was cancelled due to low-flow conditions. A clear increasing trend was observed before the summer data gap, while a decreasing trend follows it (example in Fig. 2, Latxaga). In contrast, the lowest recorded concentrations tend to occur in winter months, although in some occasions this period is slightly delayed, with lower concentrations in spring months. However, the dynamics of DS concentration in the irrigated watershed (namely Landazuria) were opposite to that observed in the non-irrigated (Fig. 2, Landazuria), with the highest concentrations recorded in late autumn to early winter and the lowest ones in summer, coinciding with the irrigation season.

The seasonal pattern in DS concentration was clearly related to the available runoff in each watershed. For both the non-irrigated and the irrigated watersheds, the high DS values correspond with the periods in which discharge is smaller, whereas the low DS values were recorded during the wet season (in the non-irrigated watersheds) or the irrigated season (in the irrigated watershed). Deviations from this seasonal pattern were observed in all watersheds in response to significantly increased discharge in the outlets (Fig. 2). In fact, the lowest DS concentrations were recorded for individual samples collected in days in which significant hydrograph peaks were also recorded. All in all, a relationship was inferred between discharge (Q) and DS concentration (Fig. 4), with significant (p<0.05) negative Spearman's ρ (-0.19 to -0.65) (Helsel and Hirsch, 2002). Oskotz Forested was the only exception with a slightly positive correlation (Spearman's ρ = +0.06) between Q and DS, although the lowest DS in this watershed were recorded for Q values over 1000 L s^{-1} (Fig. 4).

In contrast, no clear seasonal pattern was observed for SS concentrations. A visual inspection indicates that, in general, samples with high SS concentration were collected in those days experiencing a significant increase in discharge flow, although a high degree of variation was observed for any given discharge value (Fig. 3, Fig. 4). Indeed, a clear relationship between discharge and SS concentration was not detected, with more than two orders of magnitude of SS concentration recorded for almost any particular order of magnitude in discharge (Fig. 4).

Regarding the inter-annual variation, rather similar patterns were observed in DS concentration throughout the study period, although subtle differences were indeed observed. For instance, both 2011 and 2012 were quite dry in La Tejería (more than one standard deviation below the average, Table 3) which may explain the high DS concentrations recorded in 2012 (Fig. 2). In contrast, the years 2013 and 2014 were above average regarding precipitation in Oskotz, which may explain the lowest DS concentration values in the winter of 2014 (Fig. 2). Again, no clear pattern was observed for the inter-annual variability of SS concentrations. However, there were some specific periods in which the SS concentrations were systematically higher. For example, a period of high SS concentration of ca. 3-4 years was recorded in La Tejería between 2009 and 2012 (Fig. 3), while in Oskotz Forested short periods of ca. 1-2 months in some years during summer presented SS concentrations higher than those in nearby periods (Fig. 3).

3.3. Dynamics in the exported loads of dissolved solids and suspended sediment

The monthly variation in the daily exported water (Q), suspended sediment load (SSL) and dissolved solids load (DSL) is presented in Fig. 5. The dynamics in the exported loads were greatly conditioned by the availability of runoff water, especially in the case of DSL. In fact, the DSL presented a clear seasonal pattern similar to that of Q, both for typical (median) and extreme (95th percentile) hydrological conditions for every single watershed (Fig. 5). In contrast, SSL did not clearly follow the Q pattern, especially under typical conditions (median, Fig. 5). Median DSL were significantly higher than median SSL for all watersheds, being SSL negligible for most of the months (Fig. 5). Only La Tejería and, to a lesser extent, Latxaga, presented perceptible median SSL. However, SSL were severely modified when considering the 95th percentile. Perceptible loads were registered in all watersheds, with a significant contribution to the total load (i.e., both suspended and dissolved loads) in the non-irrigated watersheds (Fig. 5). In fact, Latxaga presented SSL in the same order of magnitude than DSL, whereas La Tejería presented SSL clearly higher than DSL. It is important to note that those high-flow conditions depicted here by the 95th percentile have a higher weight in determining the total annual loads. For instance, February median SSL in La Tejería was ca. 1.3 Mg day^{-1}, whereas the 95th percentile was more than 30 Mg day^{-1}.

The pattern of accumulated water yield (Q), suspended sediment load (SSL) and dissolved solids load (DSL) in relation with the accumulated time is represented in Fig. 6. These plots were constructed using only those periods for which there was information available for every variable. As a consequence, some minor bias is expected, especially in La Tejería and Latxaga, where summer periods were not sampled. In the remaining watersheds (namely Oskotz and Landazuria), the missing data is evenly distributed throughout the study period and therefore minimum bias can be expected. In the non-irrigated watersheds, there was a significant proportion of the study period in which the discharge was negligible (the gauging station had no measurable flowing water). For instance, 58% of the time was required to export 5% of the total water yield in La Tejería, 55% in Latxaga, 58% in Oskotz Principal, and 53% in Oskotz Forested, whereas 14% of the time exported 5% of total water in Landazuria (Fig. 6). In general, the accumulated dissolved load presented a pattern similar to that of the water yield, supporting the conservative behaviour of dissolved solids in water. Regarding SSL, its episodic character was clearly detectable for all watersheds. Only a 5% of the time produced 85%, 94%, 89%, 93% and 89% of the SSL in La Tejería, Latxaga, Oskotz Principal, Oskotz Forested and Landazuria, respectively (Fig. 6).

3.4. Estimation of annual suspended sediment and dissolved solids yield during the hydrological years 2007-2016

The estimated dissolved solids yield (DSY) and suspended sediment yield (SSY) for the different watershed and methods used are presented in Table 5. For dissolved solids, all methods provided consistent results. However, the regression method presented significantly biased estimates (>25%) in four out of five watersheds for suspended sediment. In fact, in comparison with other methods, regression overestimated SSY in La Tejería and Landazuria whereas it underestimated it in Latxaga and Oskotz Forested (Table 5). This fact indicates that our SSY estimation are subject to a higher degree of uncertainty than those of DSY. According to Gulati et al., (2014), regression methods are not appropriate for many agricultural streams, where pollutants concentrations and flows are not correlated.

Representative annual yield estimates (numeric integration method) are presented in Table 6. During 2007-2016, the average SSY in the studied watershed was 4.3, 1.4, 1.1, 0.9 and 0.3 Mg ha^{-1} year^{-1} for La Tejería, Latxaga, Oskotz Principal, Oskotz Forested and Landazuria, respectively, while average DSY was 1.1, 1.1, 2.2, 1.9 and 2.2 Mg ha^{-1} year^{-1}, respectively.

The highest DSY were obtained for two rather different watersheds. On the one hand, Oskotz Principal presented one of the highest water yield and one of the lowest DS concentrations. On the other hand, Landazuria presented the highest DS concentration and the lowest water yield. However, the DSY was similar in both watersheds (2.2 Mg ha^{-1} year^{-1}). The lowest DSY was estimated for the winter cereal watersheds (La Tejería and Latxaga), which presented similar values despite minor differences in water yields and DS concentrations. Intermediate values were obtained in Oskotz Forested (1.9 Mg ha^{-1} year^{-1}). The inter-annual variability in DSY for all watersheds could be explained mostly by the variability in the water yield, with rather similar CV for water and annual DSY (Table 6). In fact, the annual DSY was linearly correlated to water yield (Pearson's r between 0.91 and 0.99 for the different watersheds; Helsel and Hirsch, 2002).

Regarding SSY, it presented a considerable degree of variation that was mostly related to the differences among watersheds. Landazuria, with low slopes and semi-natural wetlands upstream from the watershed outlet (Merchán et al., 2018), presented the lowest values (0.3 Mg ha^{-1} year^{-1}), followed by both watersheds in Oskotz (0.9 – 1.1 Mg ha^{-1} year^{-1}). In these watersheds, suspended sediment loads were relatively low despite the highest slopes among the studied watersheds. The presence of forest and almost permanent coverage of soils by pastures probably influence the observed lower SSY. In contrast, the highest SSY was obtained for the winter cereal watersheds, although great differences existed among them, with La Tejería presenting ca. three times more SSY than Latxaga (4.3 and 1.4 Mg ha^{-1} year^{-1}, respectively). In a series of simulation carried out in a previous work (Casalí et al., 2008), it was found that morphology and topography played the most important role on sediment yield differences between these rainfed winter cereal watersheds.

The inter-annual variation in SSY in all watersheds was higher than that observed for DSY, as depicted by the higher CV obtained in each watershed (Table 6). Weak or non-existent linear relationship (Pearson's r between 0.13-0.59) was found between water yield and SSY. The only deviation from this pattern was found in Oskotz Forested, with a Pearson's r of 0.94 between water yield and SSY. Apparently, in this forested watershed the SS export was controlled to a higher degree by the amount of water available for runoff.

Finally, the contribution of SSY and DSY to the total yield (understood in this study as the sum of both SSY and DSY) differed greatly among watersheds. SSY represented 80%, 55%, 34%, 31% and 12% of the total yield in La Tejería, Latxaga, Oskotz Principal, Oskotz Forested and Landazuria, respectively, although these percentages were rather variable among different years (Table 6). Thus, DSY dominated in the forests/pastures and irrigated watersheds, while SSY dominated (or co-dominated) in the winter cereal watersheds.

4. Discussion

4.1. Dissolved solids concentration and loads

Dissolved solids concentrations in rivers are normally controlled mainly by the geology and the climate of the watershed (Milliman and Farnsworth, 2011). However, under similar geological/climatological conditions, the role of other factors can be detected. In fact, several authors have reported higher DS concentration in agricultural watersheds than in non-agricultural ones under similar geological/climatological conditions (e.g., Swiechowicz, 2002; Pacheco-Betancur, 2013). The increase in DS normally is associated with the presence of solutes derived from fertilizers application (such as NO_3^-), but also some other constituents (such as Ca^{2+} or Mg^{2+}) associated with increased weathering as a consequence of biogeochemical reactions between soil minerals and fertilizers (Menció et al., 2016).

In the Navarrese watersheds, the rainfed winter cereal watersheds (La Tejería and Latxaga) presented relatively similar geological/climatological characteristics. However, La Tejería (median: 547 mg L^{-1}) presented DS concentrations higher than Latxaga (median: 482 mg L^{-1}), probably as a consequence of the higher NO_3^- concentrations in

La Tejería (median: 73.5 mg L^{-1}) than in Latxaga (median: 21.0 mg L^{-1}). In fact, the higher amount of NO_3^- in La Tejería (along with some cations to compensate its negative charge) could be enough to explain the differences in DS concentration between the rainfed winter cereal watersheds.

Oskotz Principal and Forested also presented similar geological and climatological characteristics. In this case, differences in NO_3^- concentrations (medians of 9.6 mg L^{-1} and 3.6 mg L^{-1} in Principal and Forested, respectively) are not enough to justify the differences in DS concentration (Principal: 420 mg L^{-1}; Forested: 376 mg L^{-1}). In Oskotz Principal approximately one third of the watershed surface is covered by pastures and grassland that are intensively managed and grazed, which can explain the increase in concentration in relation with its more forested counterpart (i.e., the contribution of animal urine and faeces to dissolved solids concentration). In addition, there are two small villages (ca. 100 inhabitants in 2014) within the watershed whose wastewater could add some dissolved solids to the stream.

Among the Navarrese watersheds, DS concentrations were the highest in the irrigated watershed (Landazuria, median of 2275 mg L^{-1}) as a consequence of the high salinity of the soils and geological materials of the watershed (Merchán et al., 2018). In addition, the seasonal cycle in DS concentration was different from the one observed in the non-irrigated watersheds as a consequence of the dilution effect of irrigation water applied in summer. Our results are consistent with those reported for other irrigated areas in which lower DS concentrations were observed during the irrigation season (Tedeschi et al., 2001; Merchán et al., 2013). In fact, a decreasing trend in DS concentration associated with a wash out of available soluble salts is observed, as reported elsewhere (Merchán et al., 2018).

Finally, all of the Navarrese watersheds reported in this study presented: (i) a clear seasonal cycle in DS concentration; (ii) a significant negative relationship between discharge and DS concentration; and (iii) a strong relationship between annual water yield and dissolved solids yield (see section 3.2, 3.3, and 3.4). Other studies in small watersheds have reported similar seasonal variation in DS concentration (e.g., Swiechowicz, 2002; Durán-Zuaso et al., 2012), significant negative correlation between DS concentration and discharge (Llorens et al., 1997); Durán-Zuaso et al., 2012). In addition, as for the studied watersheds in Navarre, DSL mirrored the pattern observed in discharge in other studies (e.g.,Tedeschi et al., 2001; Durán-Zuaso et al., 2012; Merchán et al., 2013). In fact, this pattern is also observed in non-agricultural areas (Hubbard et al., 1990; Butler and Ford, 2017). Besides, similar observations regarding the relationship of DSY and water yield have been reported in other studies conducted at the small watershed scale (e.g., Tedeschi et al., 2001; Swiechowicz, 2002; Pacheco-Betancur, 2013).

4.2. Suspended sediment concentration and loads

According to Milliman and Farnsworth (2011) and references therein, “it is almost axiomatic to state that sediment erosion and subsequent transport are controlled by drainage basin size and topography/gradient, bedrock geology, climate (particularly precipitation/runoff), rainfall severity, vegetation cover and anthropogenic activity”. Thus, the effects of agricultural land use may be masked by a wide range of environmental conditions. However, several studies indicate that, especially under similar environmental conditions, arable land-use tend to produce higher erosion rates and sediment export (Montgomery, 2007; Cerdan et al., 2010; García-Ruiz et al., 2015).

In the case of SS, La Tejería presented the highest median concentration (0.18 g L^{-1}) followed by Latxaga (0.04 g L^{-1}), Landazuria (0.02 g L^{-1}), Oskotz Principal and Oskotz Forested (both 0.01 g L^{-1}). According with these observations, the effect of agricultural land use seems apparent, with higher SS concentration for arable watersheds and lower for those in which the soil remains covered for most of the year. Among the arable watersheds, there are important differences, with La Tejería having higher concentration for most of the statistical indicators than Latxaga or Landazuria. Several mass movements have been reported in La Tejería (Casalí et al., 2008). We hypothesize that mass movement events may be related to those higher concentrations, although, no such event was observed by local farmers in the period in which the SS concentration was higher. Regarding high SS concentration periods in Oskotz Forested (see section 3.2), they were probably related to clearing activities and rural ways maintenance in the forests within the watershed, as these activities usually take place in summer months. Such activities are expected to have minor influence in DS concentration and, in fact, no significant modification in DS concentrations are observed in Oskotz Forested during the high sediment concentration period. In a study in Finland, Nieminem et al. (2010) reported how heavy machinery used in forested areas for ditching maintenance significantly modified SS concentration but did not significantly modify dissolved constituents. In any case, despite the higher SS concentration during those works, their influence in the sediment budget of the watershed is expected to be negligible since the discharge was minimum in summer months, even reaching negligible discharge in occasions.

As in the case of DS concentration, all of the watersheds reported in this study presented: (i) a higher coefficient of variation (CV) in SS than in DS concentrations; (ii) no clear seasonal cycle in SS concentration; (iii) a weak degree of relationship between discharge and SS concentration, with 2-3 order of magnitude in SS concentration for any specific discharge; and (iv) weak or non-existent relationship between annual water yield and suspended sediment yield (see section 3.2, 3.3, and 3.4). In agreement with our results, several studies in which both variables were studied simultaneously (Llorens et al., 1997; Outeiro et al., 2010; Pacheco-Betancur, 2013) reported a CV significantly higher for SS than for DS. In addition, a huge variability in SS concentration has been reported in small watersheds in other studies (e.g., Llorens et al., 1997; Estrany et al., 2009; Pacheco-Betancur, 2013). In fact, even for larger watersheds (ca. 500 km^2), five orders of magnitude of SS concentration for any given order of magnitude in discharge have been reported (López-Tarazón et al., 2009). Besides, given the episodic nature of the SS loads (e.g., Nadal-Romero et al., 2008; Estrany et al., 2009; Durán-Zuaso et al., 2012; O'Brien et al., 2016), they are recognised to be a process much more complex than DS loads (Swiechowicz, 2002). For instance, in contrast with what happened with DSY, annual SSY was not linearly related with the annual runoff, with the exception of Oskotz Forested in which a relationship was observed between annual runoff and SSY (Pearson's r = 0.94). A feasible explanation is related with the fact that Oskotz Forested is almost fully covered by forest, which protects the soil throughout the whole year, producing the lowest sediment concentration. Thus, the amount of water leaving the watershed becomes the main explicative factor of the SS yield. Indeed, in forested watersheds in a neighbouring region north of Navarre (Basque Country) with similar characteristics than those in Oskotz Forested, the relationship of annual runoff with sediment yield was reported by Zabaleta et al. (2007). In the remaining watersheds, in contrast, other factors controlled the amount of sediment leaving the watershed. For instance, the pre-rainfall event soil moisture conditions or the season (bare soils in winter) were reported as the main controlling factors of sediment exports in Latxaga watershed (Giménez et al., 2012).

4.3. Dissolved solids and suspended sediment yield in small watersheds

Up to this point in our discussion, comparison with other studies has been made considering general patterns and processes rather than specific values or estimations. It is important to note that the results obtained in the different Navarrese watersheds may be adequately inter-compared, since they follow the same methodology over a long and similar study period. However, any comparison of our quantitative results with any other available in the literature must be considered with caveats. Among the different previous studies, there are differences in the definition of the variables (for instance, filter size for the determination of SS or constituents considered for DS computation), in the used sampling strategy (frequency, consideration of flood events sampling, simple or composite samples), in the load estimation methods (from simple interpolation to more complex methods), in the study period (what, as previously exposed, may influence estimations, especially those of SSY), etc. In fact, the lack of comparability among watersheds due to methodological issues has been manifested by other authors (e.g., Zabaleta et al., 2007; Milliman and Farnsworth, 2011; Vanmaercke et al., 2011). For that reasons, in the following sections, any comparison with other studies is intended as an illustrative example rather than an exhaustive analysis of the particular methods used and results obtained in a range of studies, which is out of the scope of this paper.

4.3.1. Dissolved solids yield in small watersheds

The vast majority of data available in the literature regarding DSY in small watersheds refers to irrigated areas. In these areas, the accumulation of salts in soils and the leaching of salt are relevant management options and therefore have received considerable attention in research studies. In fact, irrigated areas are usually located in arid and semi-arid areas where salts build up in the soils has occurred historically (e.g., Merchán et al., 2018). For instance, in irrigated areas of the Ebro River Basin (northeast Spain), even after subtracting the inputs from precipitation or irrigation, the net DSY can reach ca. 20 Mg ha^{-1} year^{-1} in flood irrigated saline soils, whereas it can be as low as 0.5 Mg ha^{-1} year^{-1} in mature pressurized irrigation systems (data compiled in Merchán et al., 2015). In comparison, scarce data is available in non-irrigated watersheds. For instance, in small watersheds in the Pyrenees (northeast Spain), DSY ranged from 0.98 to 2.3 Mg ha^{-1} year^{-1} (Nadal-Romero et al., 2012). Values of around 1 Mg ha^{-1} year^{-1} were reported for watersheds under natural (forest) or semi-natural (recolonization of shrubs and forests) conditions. Higher values were reported for high-mountain watersheds (1.7 Mg ha^{-1} year^{-1}), probably as a consequence of a higher runoff, and the maximum (2.3 Mg ha^{-1} year^{-1}) was reported for a watershed with badlands in a significant proportion of its surface. A watershed (6.7 km^2) in southern Spain with mixed land use (forest, shrubs, grassland and farms) presented 32.7 Mg ha^{-1} year^{-1} (Durán-Zuaso et al., 2012). This high value was related to the high salinity of the soils parent material. In England, 1.1 Mg ha^{-1} year^{-1} was reported by Carling (1983) in a heavily grassed, relatively undisturbed watershed (2.2 km^2).

In the Navarrese watersheds, rainfed winter cereal watersheds presented DSY values similar to that of natural or seminatural watersheds in the Pyrenees or north England. The forested watershed presented similar values to that reported for other forests in mountainous areas. The irrigated watershed presented the highest DSY of the Navarrese watersheds, but it is in the lower end of other irrigated areas, as expected for pressurized irrigation systems with an efficient use of irrigation water (Merchán et al., 2015).

Thus, the differences in DS exports between agricultural and non-agricultural watersheds are minimal, being these differences justified by other factors, mainly the salinity of soils/geological materials and the climate (section 4.1). Only in irrigated watersheds, where a huge modification of the water balance is observed (e.g., Tedeschi et al., 2001; Merchán et al., 2013; Merchán et al., 2018), a significant increase in the export of DS is expected. In this sense, agricultural land uses expected to increase water yield (such as a shift from forested to arable land, or from rainfed to irrigated agriculture) would increase the DS exports (Scanlon et al., 2007).

4.3.2. Suspended sediment yield in small watersheds

In small watersheds (0.3 – 2.8 km^2) in the Pyrenees, SSY ranged from 0.35 to 147 Mg ha^{-1} year^{-1} (Nadal-Romero et al., 2012). Natural (high mountain or forests) or semi-natural (recolonized by shrubs and forests) watersheds presented 0.35 – 0.54 Mg ha^{-1} year^{-1}, while the extreme 147 Mg ha^{-1} year^{-1} value was reported for a watershed severely affected by badlands. Also, forested watersheds (3 – 48 km^2) in the Basque Country presented 0.15 – 0.31 Mg ha^{-1} year^{-1} (Zabaleta et al., 2007). In England, 0.2 Mg ha^{-1} year^{-1} was reported by Carling (1983) in a heavily grassed, relatively undisturbed watershed (2.2 km^2). In Can Revull, a small agricultural watershed in Mallorca, Spain (ca. 1 km^2), SSY averaged 0.03 Mg ha^{-1} year^{-1} (Estrany et al., 2009). This low value (even lower than in forested watersheds) was justified by a combination of retention structures (terraces and sloping walls), and the limited connectivity associated to the concave topography of the watershed. In a flood-irrigated watershed in the Middle Ebro Valley, SSY was 0.2 Mg ha^{-1} year^{-1} (Lasanta et al., 2001). This value is rather similar to that obtained in this study for the irrigated watershed (Landazuria, 0.3 Mg ha^{-1} year^{-1}). In five small agricultural (pasture and arable land) watersheds (3.3 – 11.5 km^2) in Ireland, Sherriff et al. (2015) reported 0.09 – 0.25 Mg ha^{-1} year^{-1} for SSY. These values are one order of magnitude lower than those obtained in the present study. The authors justify the low values of its estimates with the characteristics of these agricultural areas: “high landscape complexity, comprising small and irregularly shaped fields, separated by a dense network of hedgerows and vegetated ditches” (Sherriff et al., 2015). In contrast, in 12 small watersheds (2.5 – 40 ha) in Australia, estimated SSY was 0.8 Mg ha^{-1} year^{-1} (range: 0.2 – 1.5; n=3) for forest, 2.2 Mg ha^{-1} year^{-1} (range: 1.6 – 3.6; n=6) for pasture and 3.1 Mg ha^{-1} year^{-1} (range 2.7 – 3.5; n=3) for crop land uses (Mahmoudzadeh et al., 2002). The values reported in Australia for the different land uses are similar to those obtained in the Navarrese watersheds.

In this context, the estimated values in the Navarrese forested watershed (Oskotz Forested) were higher than in other forested watershed in northern Spain. Results from the terraced watershed in Mallorca or the Irish watersheds are not comparable with our results for arable land due to the severe differences in the land management. Indeed, our results for arable land (1.4 – 4.3 Mg ha^{-1} year^{-1}) are one order of magnitude higher than the results reported for England, Mallorca, and Ireland (Carling, 1983; Estrany et al., 2009; Sherriff et al., 2015). In contrast, the results reported for the Australian watersheds (Mahmoudzadeh et al., 2002) are coherent with those obtained in this study.

A wide range of variation has been reported in small watersheds SSY both for non-agricultural and agricultural watersheds. Within non-agricultural watersheds, the presence of badlands is associated with the highest reported SSY, although in most of the cases, the SSY values reported for natural areas (or for abandoned cropland) are lower than those reported for currently productive agricultural areas. Within agricultural watersheds, there is also a huge variation in the reported values that are justified either by natural factors (such as the differences in the shape of the Navarrese watersheds La Tejería and Latxaga, Casalí et al., 2008) or by management factors (presence of hedgerows or vegetated ditches, Sherriff et al., 2015).

4.3.3. Contribution of dissolved solids or suspended sediment to total loads

Among those studies conducted in small watersheds in which both SS and DS have been assessed, DS contribution tended to dominate the total exported loads. For instance, in a small (36 ha) terraced agricultural watershed that had been abandoned, the estimated DSY (0.15 Mg ha^{-1} year^{-1}) was almost four times higher than SSY (0.04 Mg ha^{-1} year^{-1}) (monitoring time: 1.5 years; Llorens et al., 1997). DSY contributed to 80% of total yield in a heavily grassed watershed (2.2 km^{2}) in north England (Carling, 1983). In a flood-irrigated agricultural watershed (643 ha) 98% of the total load was in soluble form (Lasanta et al., 2001). Both Swiechowicz (2002) and Duran-Zuaso et al. (2012) reported DS loads as 95% of total loads in mixed land use (shrubs, forest and agricultural) watersheds (22.4 and 6.7 km^{2}, respectively). Pacheco-Betancur (2013) analysed a watershed with two hydrological stations, one of them draining mainly forest whereas the second one was mainly arable land. This author found that DS dominate the total load in both the forested and the arable area. In a comprehensive assessment of four watersheds in the Pyrenees considering dissolved, suspended and bed loads, Nadal-Romero et al. (2012) reported the dominance of DS in the exported loads for the Arnás (natural shrubs and forest colonization, 61% DS), Izas (high-mountain grasslands, 70% DS) and San Salvador (natural forest, 74% DS). Only a watershed severely affected by badlands (26% of its surface) presented dominance of SS (Araguás, 95% SS, Nadal-Romero et al., 2008, 2012).

As can be seen, most of the available studies in the literature were conducted in natural or semi-natural areas. Our results on agricultural watersheds (section 3.4) in combination with the literature reviewed suggest a shift in the dominance from DS to SS in the exported loads in small watersheds. This shift is consistent with the higher SS exports expected in arable lands (e.g., Montgomery, 2007; Cerdan et al., 2010; García-Ruiz et al., 2015) while DS exports are not severely modified under arable land use (unless the watershed under consideration is irrigated, as elaborated in previous paragraphs).

Indeed, as Milliman and Farnsworth (2011) reported for high-order rivers, “it is the difference in physical delivery (or lack thereof) of sediment that seems to be the key factor in determining whether a river is sediment- or dissolved-dominated”.

4.4. Final reflections and remarks

In this study, our focus has been on the effects of agriculture on the export of dissolved solids and suspended sediment at the small watershed scale. However, from the presented discussion it is clear that the specific characteristics of the watersheds, normally associated to non-controllable factors, play a huge role in the DS and SS export processes as previously discussed. An example of such processes is available in a study conducted in small watersheds (168-339 ha) in the Tianshan Mountains, northwestern China. In this study, watersheds with glaciers influence (one-third of the watershed surface) presented rather higher SSY (ca. seven-fold) and DSY (ca. two-fold, similar to water yield) than watersheds without glacier influence (Gao et al., 2014). The differences were attributed to the huge erosive power of glaciers (abrasion, exposure of soils, etc.) that provides abundant easily erodible sediment and increases the effective surface for chemical attack (Gao et al., 2014). In this sense, it is important to understand that although agricultural land use is expected to modify the DS and SS dynamics in particular ways, in some occasions the variability imposed by the wide range of natural conditions in a watersheds may be enormous.

In addition, it is noteworthy that although SS and DS concentration are usually not related, some degree of relationships is expected between both variables. Indeed, chemical and mechanical erosion processes enhance each other: on the one hand, crushed rock provides an increase in chemically reactive surface; on the other, weathered rocks are more easily fractured (Louvat and Allègre, 1997). This is true especially in watersheds with highly soluble and erodible materials. For instance, Tillman and Anning (2014) reported SS concentration as an explanatory variable for DS concentration in the Colorado River, although this relationship was significant only for sub-watersheds with a high proportion of geological materials which were both soluble and erodible (e.g., marls). As an extreme example, a significant proportion (>65%) of SS generated in saline and sodic soils is expected to dissolve in water as the stream order increases (Cadaret et al., 2016). Despite this, a typically made assumption is that chemical weathering supplies the dissolved load to rivers whereas mechanical erosion supplies the solid load. However, this assumption fails in watersheds with erodible and soluble materials in which suspended sediment detached has a significant soluble fraction that eventually contributes to the dissolved solids fraction.

Although this study has been conducted at the small watershed scale, the dynamics of DS and, particularly, SS are highly scale-dependant. From plot studies to large watersheds, controlling processes may change. On the one hand, plot scale export of dissolved and suspended loads is mainly controlled by the interaction of climate characteristic such as rain intensity, soil and/or geological properties, land use and agricultural management. On the other hand, a mixture of climatic conditions, soils, geologic materials, river morphology, etc., makes difficult to relate patterns in DS or SS behaviour to specific characteristics in regional watersheds. In these sense, Vanmaercke et al. (2011) compiled previously published data at the European scale and found that SSY presented a significant negative relationship with watershed area, although this relationship was quite variable when considering different climates, selected watershed sizes, etc. In agreement with this idea, a compilation of data from over 1500 large rivers by Millimand and Farnsworth (2011) indicated that the ratio SSY/DSY decreased with increasing watershed size, probably as a consequence of downstream storage of suspended sediments. Tiwari et al. (2017) showed how scale effects in dissolved constituents imply that streams tend to lose headwater chemical characteristics and that the spatial variability is reduced as small headwaters from heterogeneous landscape patches converge and the contribution of groundwater shifts from shallow to deep-origin.

In addition, anthropogenic factors such as land use or the degree of regulation in the rivers is paramount in its SS and DS dynamics. For instance, a highly regulated watershed (Ebro, north-eastern Spain) presented a marked sediment deficiency (Tena et al., 2011), with SSL an order of magnitude lower than DSL (Négrel et al., 2007), whereas low- or non-regulated watersheds presented similar orders of magnitude with, in general, SS dominance (e.g., Singh et al., 2008). In contrast, the effect of regulation in DSL consist mainly in a buffering of the load, with relatively constant concentrations and loads throughout the year downstream from reservoirs (Ahearn et al., 2005), although some decrease in the load is expected as a consequence of water abstraction.

5. Conclusions

From the presented data in the Navarrese watersheds and that available in the literature, the effects of agricultural land use in the dynamics of concentrations and exported loads of DS and SS at the small watershed scale can be summarized as follows:

- The temporal dynamics of SS and DS concentration and loads are controlled by the fact that SS is composed by particles mobilized mostly under high flow conditions whereas DS are conservative with water, i.e., their dynamics are associated to that presented by water. As a consequence, SS concentrations and loads are extremely variable, depending on many factors (such as watershed size and topography, bedrock geology, climate, rainfall severity, vegetation cover, anthropogenic activity) while DS concentration and loads are mostly controlled by the geological/climatological characteristics of the watershed and consequently follow a seasonal cycle. There are no important differences in these temporal dynamics among different land uses, as depicted by the similar general behaviour in a range of agricultural and non-agricultural land uses both in the Navarrese watersheds and in the literature.

- Agricultural land use seems to increase the DS concentration in the drainage water, probably due to the contribution of dissolved constituents via fertilizers or livestock excreta and a more easily chemical weathering of tilled soils. However, the variability among watersheds imposed by natural factors (such as salinity of soils/geological materials or climate) is usually higher than the effect of agricultural land use. Regarding DS loads, no clear pattern is observed since it is mainly controlled by the water yield dynamics. In this sense, agricultural land uses expected to increase water yield (such as a shift from forested to arable land, or from rainfed to irrigated agriculture) would increase the DS exports.
- In general, agricultural land use increases SS concentration and loads in watersheds, although the magnitude of this effect depends on many other factors, both natural (climatic characteristics, vegetation cover, etc.) and anthropogenic (agricultural system, management practices, etc.). The combination of uncovered soils of arable land in watersheds with characteristics favourable for sediment transport propitiates the highest reported sediment yield (only surpassed to that reported in watersheds severely affected by badlands). In contrast, covered soils in non-arable land (either pastures or forests) present relatively low sediment export.
- The variability of DS yield among watersheds with different characteristics (including land use) is mainly explained by differences in water yield, and it is lower than that of SS yield. Out of the total yield (DS + SS), DS yield normally dominates under non-agricultural and agricultural land uses. However, SS yield becomes dominant under watersheds with predominantly arable land and environmental conditions that facilitate sediment export. In fact, the differences in sediment delivery (or lack thereof) seems to be the key factor in determining if a watershed export is dominated by SS or DS.

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Table 1. Available data for the present study in the network of agricultural watersheds (Government of Navarre).

Watershed	**Climate** (type and avrg. rainfall & temperature)	**Surface** (ha)	**Land use** (type and percentage)	**Discharge data** (hydrol. years)	**Water quality data** (number of daily samples)
La Tejería	Humid sub-Mediterranean 755 mm 12.3 ºC	169	Arable land, 93% Pastures, 2% Others, 5%	1998-2016	4153 (≈ 219/year)
Latxaga	Humid sub-Mediterranean 861 mm 11.8 ºC	207	Arable land, 85% Pastures, 11% Others, 4%	1998-2016	4112 (≈ 216/year)
Oskotz, principal	Sub-Atlantic 1278 mm 10.6 ºC	1688	Forests, 61% Pastures, 23% Arable, 13% Others, 3%	2001-2016	4073 (≈ 255/year)
Oskotz, forested	Sub-Atlantic 1278 mm 10.6ºC	434	Forests, 83% Arable, 11% Pastures, 5% Others, 1%	2001-2016	4339 (≈ 271/year)
Landazuria	Dry Mediterranean 417 mm 13.2 ºC	480	Irrigated crops, 53% Rainfed cereals, 35% Others, 12%	2007-2016	3014 (≈301/year)

Table 2. Number of samples in which suspended sediment (SS), anions and cations were determined; multi-linear regression coefficient of determination (R^2) and Dissolved Solids (DS) equation for each watershed (all constituents in mg L^{-1}).

Watershed	SS	Anions	Cations	R^2	Equation
La Tejería	4109	4145	3239	0.988	$DS = 15.37 + 1.46\cdot Cl^- + 1.39\cdot SO_4^{2-} + 1.30\cdot HCO_3^- + 1.23\cdot CO_3^{2-} + 1.23\cdot NO_3^-$
Latxaga	3977	4103	3159	0.990	$DS = -1.32 + 1.66\cdot Cl^- + 1.38\cdot SO_4^{2-} + 1.31\cdot HCO_3^- + 1.08\cdot CO_3^{2-} + 1.30\cdot NO_3^-$
Oskotz Princ.	4009	4071	2800	0.980	$DS = 13.77 + 2.40\cdot Cl^- + 1.65\cdot SO_4^{2-} + 1.25\cdot HCO_3^- + 2.05\cdot CO_3^{2-} + 1.11\cdot NO_3^-$
Oskotz For.	4254	4320	3081	0.981	$DS = 7.91 + 1.43\cdot Cl^- + 1.30\cdot SO_4^{2-} + 1.31\cdot HCO_3^- + 1.29\cdot CO_3^{2-} + 1.29\cdot NO_3^-$
Landazuria	2961	2982	1722	0.984*	$DS = 88.61 + 1.56\cdot Cl^- + 1.31\cdot SO_4^{2-} + 1.25\cdot HCO_3^- + 1.30\cdot NO_3^-$

* For Landazuria the statistical model did not considered estimated CO_3^{2-} concentration in the regression.

Table 3. Precipitation values (mm) in each watershed, range of standardized values for the hydrological years (Oct-Sep) 2007-2016.

Hydrol. Year	**La Tejería**	**Latxaga**	**Oskotz**	**Landazuria**	**Standardized values range**
2007	860	982	1246	445	-0.44 to +0.31
2008	895	841	1179	375	-0.65 to +0.47
2009	682	939	1242	400	-0.52 to -0.04
2010	790	798	1105	400	-0.88 to -0.02
2011	551	600	n.a.	402	-1.23 to -0.27
2012	531	709	1121	302	-1.52 to -0.83
2013	1324	1665	2148	617	+2.32 to +2.50
2014	816	1162	1658	405	-0.22 to +0.82
2015	849	1039	1594	496	+0.26 to +0.92
2016	636	765	1224	386	-0.73 to -0.47
Average ± S.D.	793 ± 216	950 ± 285	1391 ± 326	423 ± 80	

S.D.: Standard Deviation; Standardized value = (x_i-x_{avg})/S.D.; n.a.: not available (failure in recording systems during 12 days).

Table 4. Selected statistics of daily average discharge (Q, $L\ s^{-1}$), suspended sediment (SS, $g\ L^{-1}$) and dissolved solids (DS, $mg\ L^{-1}$) concentration in the studied watersheds for the hydrological years (Oct-Sep) 2007-2016.

Watershed	**La Tejeria**			**Latxaga**			**Oskotz Principal**			**Oskotz Forested**			**Landazuria**		
Variable	Q	SS	DS	Q	SS	DS	Q	SS	DS	Q	SS	DS	Q	SS	DS
N	3653	2528	2532	3653	2412	2425	3653	3188	3190	3653	3043	3040	3653	2961	2982
Perc. 05	0	0.007	429	0	<0.005	390	0	<0.005	279	0	<0.005	256	5	<0.005	1620
Quar.1	0	0.042	494	0	0.017	440	9	0.005	376	3	<0.005	300	8	0.010	1960
Median	1	0.182	547	2	0.038	482	76	0.012	420	19	0.012	327	12	0.024	2275
Quar. 3	10	1.078	612	12	0.103	529	280	0.028	475	70	0.029	355	17	0.053	2547
Perc. 95	52	4.536	713	80	0.632	629	1512	0.221	577	415	0.183	388	30	0.304	2918
Perc. 99	170	10.193	768	220	1.788	722	4120	0.762	637	1047	0.516	415	63	1.095	3051
Maximum	625	33.484	1075	553	61.000	1066	10788	10.003	958	2840	5.010	462	545	18.268	3534
IQR	10	1.04	119	12	0.086	89	271	0.023	99	67	0.026	55	9	0.043	587
Average	12	1.05	556	16	0.16	492	342	0.05	426	89	0.04	326	15	0.090	2259
S.D.	34	2.33	89	41	1.28	79	821	0.25	87	215	0.16	42	17	0.468	397
C.V. (%)	284	221	16	251	784	16	240	469	20	242	355	13	117	522	18
Avrg./Median	8.08	5.79	1.02	8.45	4.25	1.02	4.51	4.61	1.01	4.73	3.55	1.00	1.26	3.74	0.99

N: number of data; Perc.: Percentile; Quar.: Quartile; IQR: inter-quartile range; S.D.: standard deviation; C.V.: coefficient of variation.

Table 5. Results from different methods for load estimations. SSY and DSY refers to suspended sediment yield and dissolved solids yield, respectively. All values in Mg ha^{-1} year^{-1}.

Estimation method	**La Tejería**		**Latxaga**		**Oskotz Principal**		**Oskotz Forested**		**Landazuria**	
	SSY	DSY	SSY	DSY	SSY	DSY	SSY	DSY	SSY	DSY
Numeric Integration	4.26	1.07	1.39	1.12	1.14	2.24	0.85	1.88	0.29	2.17
Regression	8.12*	1.06	1.00*	1.11	0.93	2.24	0.48*	1.91	1.75*	2.16
Ratio Estimator	4.46	1.06	1.46	1.10	1.22	2.21	0.82	1.84	0.31	2.13

* The software used for regression (USGS LOADEST) warns about the high bias of these estimations.

Table 6. Runoff (mm), suspended sediment yield (SSY, Mg ha^{-1}) and dissolved solids yield (DSY, Mg ha^{-1}) for the studied watersheds during the hydrological years 2007-2016. Presented yields were computed by numerical integration method (see Table 5).

	La Tejería			Latxaga			Oskotz Principal			Oskotz Forested			Landazuria		
	Runoff	SSY	DSY	Runoff	SSY	DSY	Runoff	SSY	DSY	Runoff	SSY	DSY	Runoff	SSY	DSY
2007	256	1.6	1.4	234	1.4	1.1	802	1.0	3.3	571	1.1	1.8	130	0.3	3.2
2008	177	2.1	0.8	201	0.5	0.9	575	0.5	2.1	543	0.6	1.7	79	0.1	1.9
2009	267	8.3	1.3	287	5.7	1.4	563	1.2	2.1	727	0.7	2.3	92	0.1	2.5
2010	161	6.1	0.8	185	0.4	0.9	507	1.7	1.8	502	0.4	1.5	89	0.0	2.2
2011	72	2.3	0.4	127	0.2	0.6	348	1.3	1.3	357	0.3	1.0	85	0.1	1.8
2012	4	0.1	0.0	38	0.1	0.2	346	0.2	1.3	353	0.2	1.2	42	0.0	0.9
2013	415	11.4	1.9	513	2.6	2.2	1151	2.8	3.8	1275	2.5	3.7	143	0.2	3.1
2014	219	1.2	1.1	344	1.5	1.5	712	0.1	2.0	704	0.8	1.9	94	1.6	1.8
2015	269	2.5	1.2	316	1.2	1.3	768	2.2	2.4	790	1.4	2.0	133	0.4	2.5
2016	382	7.0	1.8	249	0.3	1.1	620	0.5	2.2	639	0.6	1.7	96	0.0	1.8
Average	222	4.3	1.1	250	1.4	1.1	639	1.1	2.2	646	0.9	1.9	98	0.3	2.2
S.D.	126	3.7	0.6	129	1.7	0.5	238	0.9	0.8	265	0.7	0.7	30	0.5	0.7
C.V. (%)	57	87	55	52	123	49	37	76	36	41	83	39	30	172	32
Contribution to: (DSY + SSY)	-	80%	20%	-	55%	45%	-	34%	66%	-	31%	69%	-	12%	88%

S.D.: Standard deviation; C.V.: Coefficient of variation.

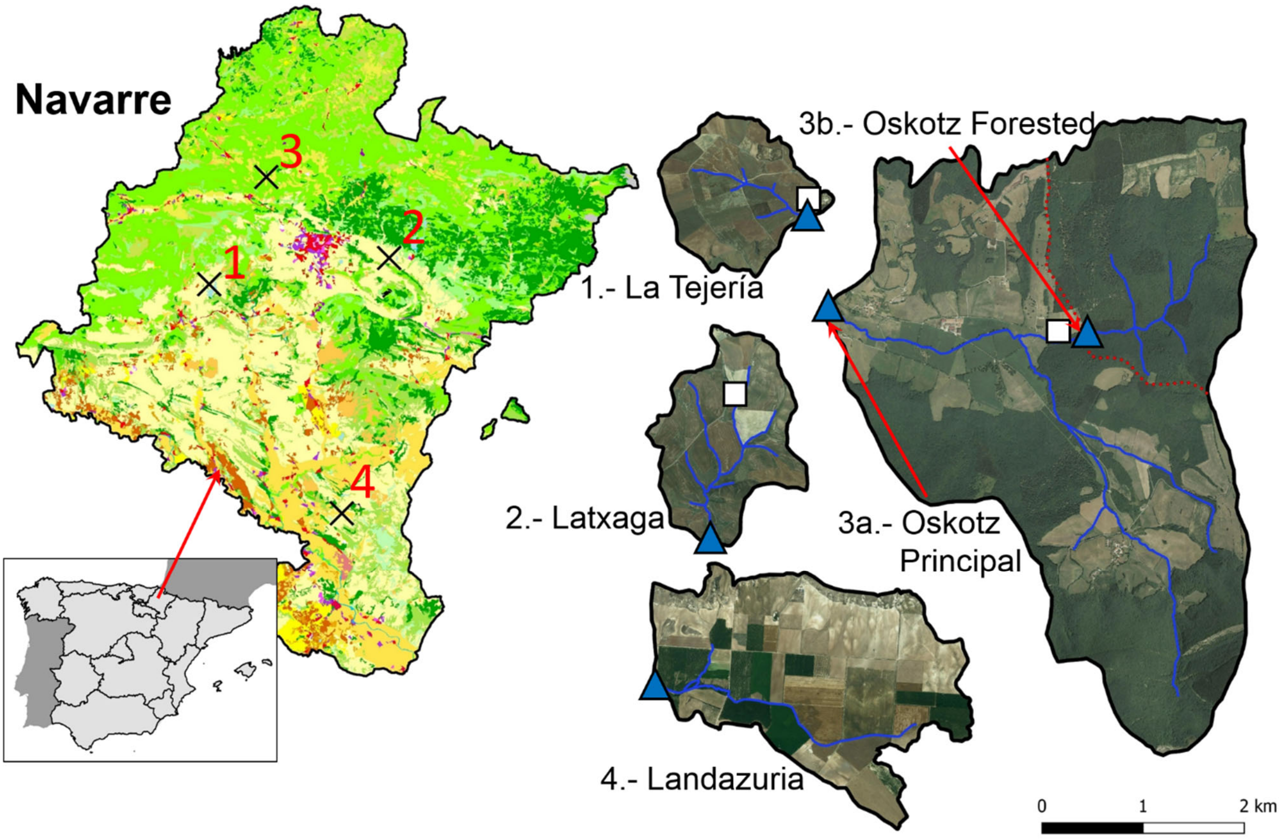

Figure 1. Land uses in Navarre (Spain) [Source: CORINE Land Cover 2012, standard legend] and experimental watersheds (black crosses in Navarre map) monitored by the Government of Navarre. In each watershed (ortophotos taken in summer 2017), the hydrological station (blue triangle) and meteorological station (white square) are depicted. In Landazuria, the meteorological station is 5 km south from the watershed. Note that both Oskotz Principal and Forested watersheds share the same meteorological station.

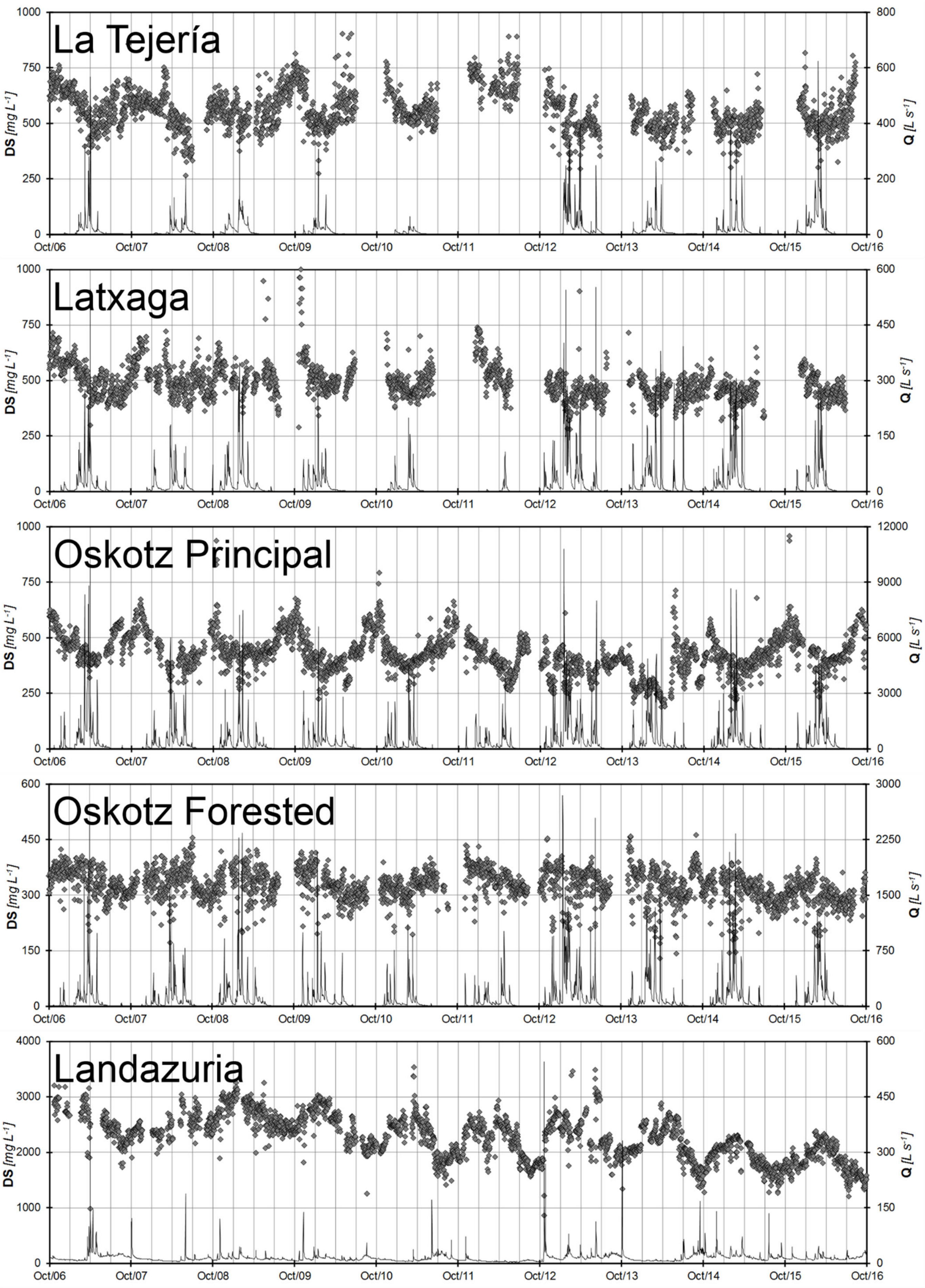

Figure 2. Daily dissolved solids concentration (DS) and discharge (Q) in the Navarrese watersheds during the hydrological years 2007-2016.

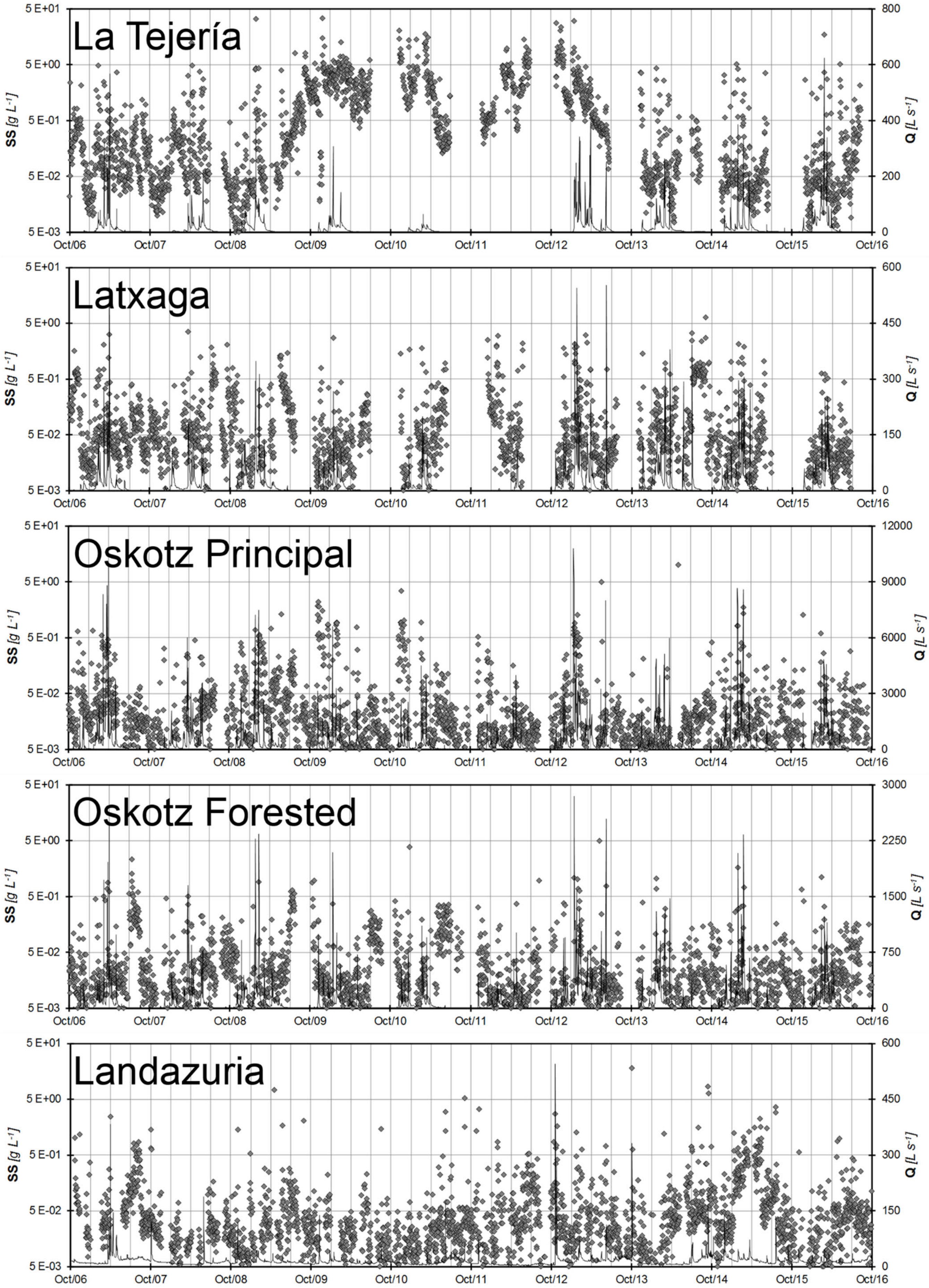

Figure 3. Daily suspended sediment concentration (SS) and discharge (Q) in the Navarrese watersheds during the hydrological years 2007-2016. Note the logarithmic scale in SS axis.

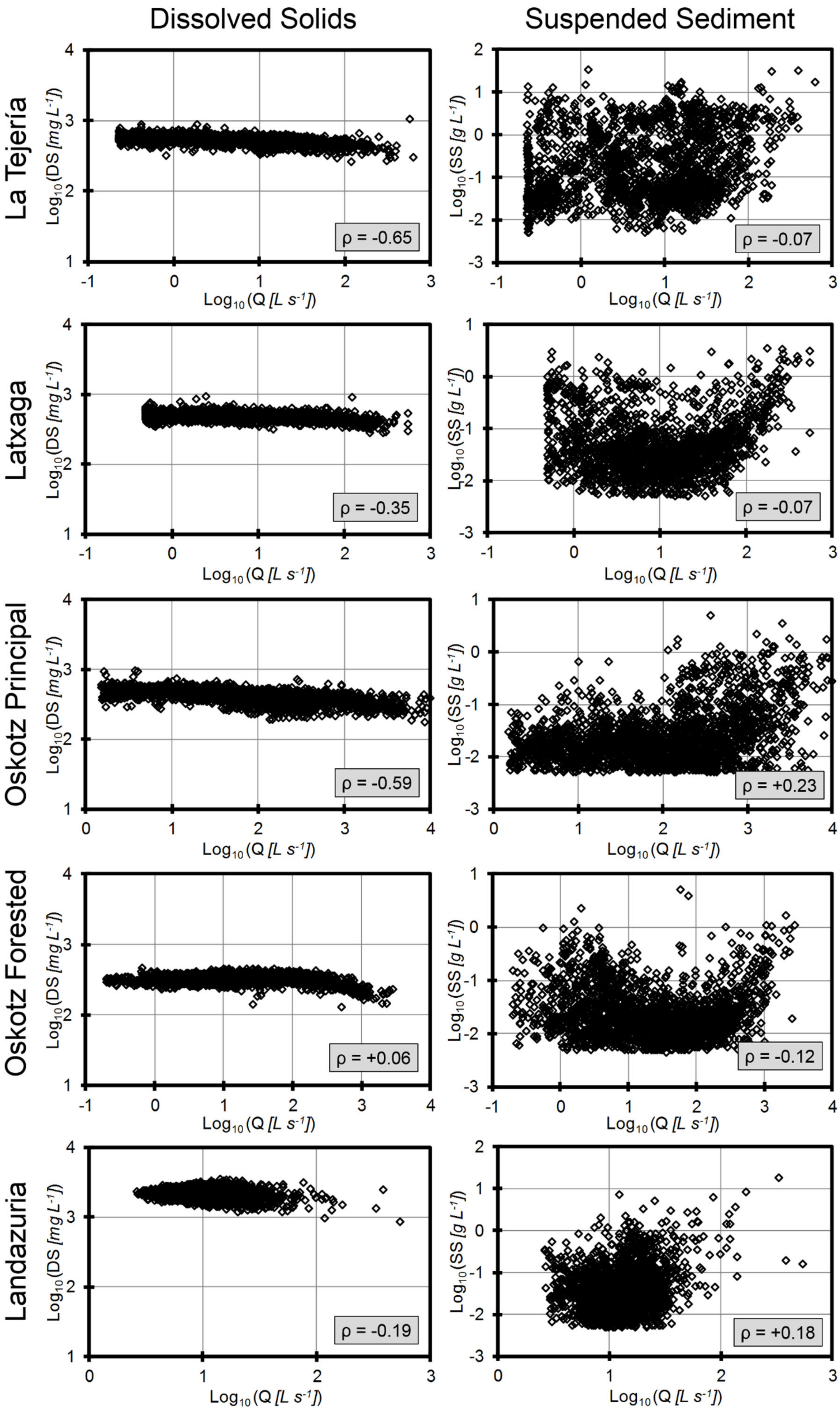

Figure 4. Relationship (double-logarithmic scale) between discharge (Q) and the concentration of dissolved solids (DS) and suspended sediment (SS) in the Navarrese watersheds. The degree of correlation ($p < 0.05$) between variables is indicated by the Spearman's ρ (Helsel and Hirsch, 2002).

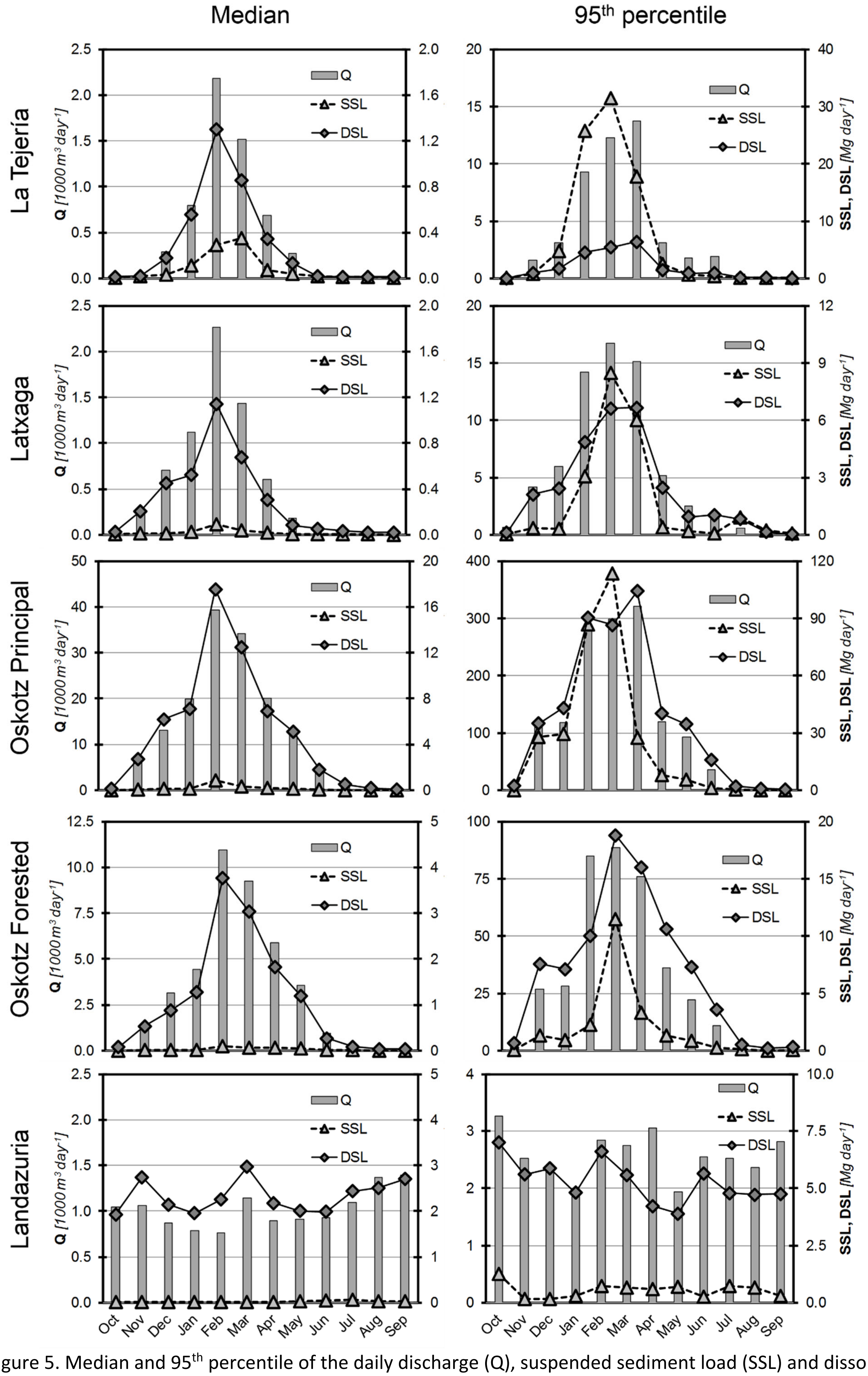

Figure 5. Median and 95th percentile of the daily discharge (Q), suspended sediment load (SSL) and dissolved solids load (DSL) in the Navarrese watersheds.

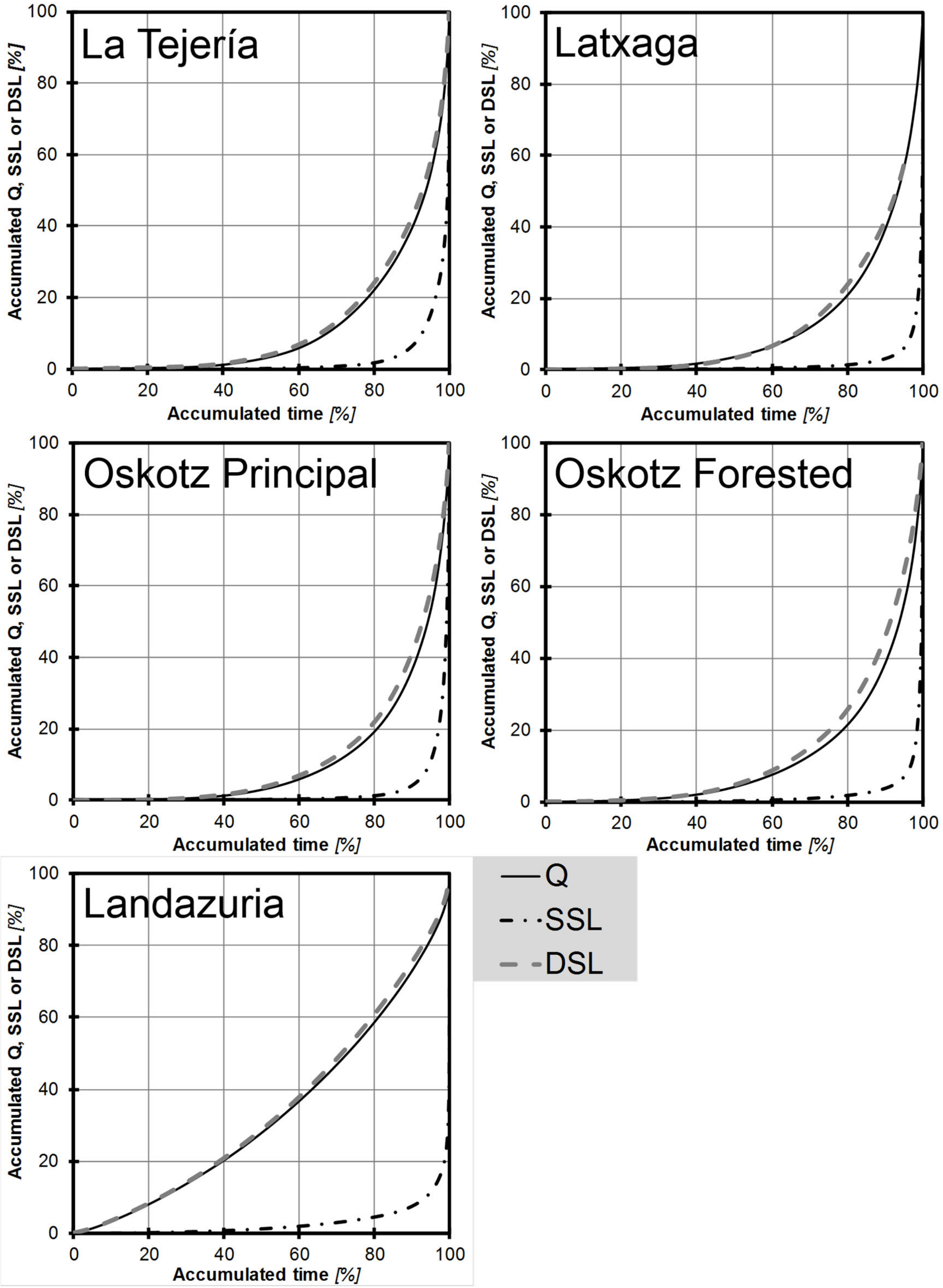

Figure 6. Accumulated discharge (Q), suspended sediment loads (SSL) and dissolved solids loads (DSL) *versus* accumulated time in the Navarrese watersheds.