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Short Communication

Connection between El Niño-Southern Oscillation events and river nitrate concentrations in a Mediterranean river

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A B S T R A C T

The causes of interannual nitrate variability in rivers remain uncertain, but extreme climatic events have been suggested as drivers of large nitrate inputs to rivers. Based on a 24-year data set (1983–2006), we suggest that El Niño-Southern Oscillation (ENSO) can affect nitrate behavior in a seasonal extra-tropical stream, the Llobregat (NE Iberian Peninsula), located thousands of kilometers away from the ENSO oscillating system via atmospheric teleconnections. Two commonly used indices, the Southern Oscillation Index (SOI) and the self-calibrating-Palmer Drought Severity Index (scPDSI) showed highly significant correlations with nitrate concentrations, which recurrently increased during La Niña phases, coinciding with severe droughts.

1. Introduction

During the 20th century, the global nitrogen (N) cycle has been severely disturbed, causing N enrichment of terrestrial and aquatic ecosystems (Schindler, 2006; Sutton et al., 2011). Nitrate leaching from river catchments is a useful indicator of N cycle disruption (Goodale et al., 2003; Gundersen and Bashkin, 1992). Today, high nitrate levels in freshwater bodies remain an important pollution target worldwide with implications for human and environmental health (Skeffington, 2002). A large body of published work assesses nitrate sources, concentrations fluxes and behavior, trying to understand its spatial and temporal behavior. However, its variability is still not thoroughly understood. While the causes of spatial and short-term (seasonal, annual) variations in freshwater nitrate concentrations are reasonably well known, the drivers of long-term (interannual, decadal) trends remain uncertain (de Wit et al., 2007; Stålnacke et al., 2003). Climatic factors have been suggested as potential causes of large interannual variations in nitrate concentration and export. Documented impacts of drought on stream biogeochemistry include reduced nitrate concentrations (Foster and Walling, 1978) due to reduced contribution of the catchment, with major flushes of nitrates to surface waters driven by storm events when drought ends, (Morecroft et al., 2000). Other studies reveal relationships of nitrate concentrations with the temperature-warming trend of last decade mediated by biological (Zweimüller et al., 2008) and geological processes (Baron et al., 2009). Recent investigations in the Northern Hemisphere have suggested some links between freshwater nitrate variations and the general atmospheric circulation systems. In the UK, synchronous patterns of variation in nitrate concentration observed in upland freshwaters showed significant correlations with the Northern Atlantic Oscillation's (NAO) index winter values (Monteith et al., 2000). Other studies on Swedish and Swiss lakes showed similar outstanding relationships between the NAO and nitrate concentrations (Straile et al., 2003; Weyhenmeyer, 2004). In a l6-year study conducted in Canada, the highest nitrate levels in upland streams were recorded after the strong La Niña episode of 1989 (Watmough et al., 2004). Hence, a more or less general pattern of interannual variability of nitrate concentrations and export is beginning to emerge in northern temperate areas, likely driven by low-frequency atmospheric modes (NAO, ENSO). More recently Marcé et al. (2010) found strong and consistent signatures of ENSO in the inflow and oxygen content of a reservoir located in the Northeast of the Iberian Peninsula (IP).

Our present research focuses on how selected climatic variables (precipitation, drought, atmospheric and sea surface temperature) influence river nitrate variations in time and which teleconnections are central to modulate these relationships in the northeast of the IP. To our knowledge, this approach has rarely been attempted before, and it should be taken into account as it has been demonstrated that a number of low-frequency Atlantic and European atmospheric modes (NAO,

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ENSO, Mediterranean Oscillation, Western Mediterranean Oscillation, East Atlantic and Scandinavian patterns) affect precipitation/drought patterns on the IP, at different spatial and temporal scales (Barnston and Livezey, 1987; González-Hidalgo et al., 2009; Rodríguez-Puebla et al., 1998; Wibig, 1999).

The present paper is a preliminary analysis of a long-term data set (1983–2006) showing significant correlations of nitrate concentrations in river water with drought and precipitation patterns, as well as with both ENSO phases (La Niña and El Niño) in a Mediterranean river. Some hypotheses on the potential underlying physical mechanisms that could explain these relationships are also provided, in order to guide future research. ENSO teleconnections are known to be influential on the Iberian Peninsula climate by modifying the magnitude and frequency of precipitation, in a heterogeneous manner (Rodó et al., 1997; Rodríguez-Puebla et al., 1998). Indeed, some areas are affected by severe droughts during the final months of La Niña years and the initial months of the following year, whereas other regions are affected by dry conditions during the first months of El Niño years, as well as during the summer and autumn of the following year (Muñoz-Díaz and Rodrigo, 2005; Vicente Serrano, 2005). The dynamics of the ENSO-Mediterranean teleconnections is still poorly known, although several explanatory mechanisms have been proposed (Klein et al., 1999; Marshall et al., 2001; Shaman and Tziperman, 2011; Sutton et al., 2000; Trenberth and Hurrell, 1994).

2. Materials and methods

The Llobregat River system drains a large part of Catalonia, at the north-eastern Iberian Peninsula, its basin comprising 4957 km^2 (Fig. 1). The climate is of the Mediterranean type, characterized by intense summer droughts and a remarkable, interannual variability in precipitation patterns. In this region, rainfall of torrential nature concentrates in autumn and the month of December (Martín-Vide et al., 2008). Average precipitation in the Llobregat basin ranges from <550 to 900 mm/yr. The mean annual river discharge is bimodal and highly variable, with maxima recorded in May and December. The basin is subjected to intense human activity and several sewage treatment plants are active at present, but its catchment is not targeted as a nitrate vulnerable zone (European legislation, Nitrate Directive) by the official management agency (ACA, 2007, 2011).

For this study, we used the public database of the Catalonian Water Agency (ACA, 2007, 2011). Of the 11 sampling stations in the Llobregat watershed, only two provided suitable long-term nitrate time series (continuous sampling and less than 10% of data missing); these are located in the middle (Castellbell i El Vilar: CieV) and lower (Sant Joan Despí: SJD) reaches, respectively. Nitrate (NO_3) concentrations were measured by spectrophotometry (Clescerl et al., 1985–2005). Monthly nitrate time series was compared with available river discharge ($m^3\,s^{-1}$) time series (1990–2004) in the two selected sampling stations, in order to derive potential statistical correlations. Precipitation data were obtained from 26 stations of the Spanish Meteorological Service (AEMET) network (1983–2006). We applied the World Meteorological Organization (WMO) recommendations for quality control (Aguilar et al., 2003) and tested the homogeneity with the Standard Normal Homogeneity Test (Alexandersson and Moberg, 1997). Monthly series of accumulated precipitation were calculated to correlate with monthly nitrate series. To compare precipitation and nitrate series, regional time series of precipitation have been constructed by averaging daily anomalies (Jones and Hulme, 1996) and separating climate series into climatology and anomaly components. Drought conditions were identified using the self-calibrated Palmer Drought Severity Index — scPDSI (Wells et al., 2004), which has been used in the past to study summer moisture across Europe (van der Schrier et al., 2006). The scPDSI data (1983 to 2002) were obtained from the Climate Research Unit, University of East Anglia.

To characterize ENSO phases, we utilized the Southern Oscillation Index (SOI), calculated as the series of standardized differences in monthly standardized sea level pressure (SLP) between Tahiti and Darwin (Rasmusson and Carpenter, 1982; Ropelewski and Jones, 1987). Available monthly values of SOI (1983–2006) were obtained from the Climate Research Unit (East Anglia University). We used the 5-month running mean values of the SOI remaining below -0.5 standard deviations for 5 months or longer for the El Niño phases, and over $+0.5$ standard deviations for 5 months or longer for the La Niña events (Rasmusson and Carpenter, 1983; Ropelewski and Halpert, 1996; Vicente-Serrano, 2005). The 1980s and 1990s included eight El Niño (1982/83, 1986/87, 1991–1993, 1994/95, 1997/98, 2002, 2004, 2006), five La Niña episodes (1984/85, 1988/89, 1995/96, 1999, 2000) and two of the strongest El Niño episodes of the century (1982/83 and 1997/98), as well as a set of consecutive periods of

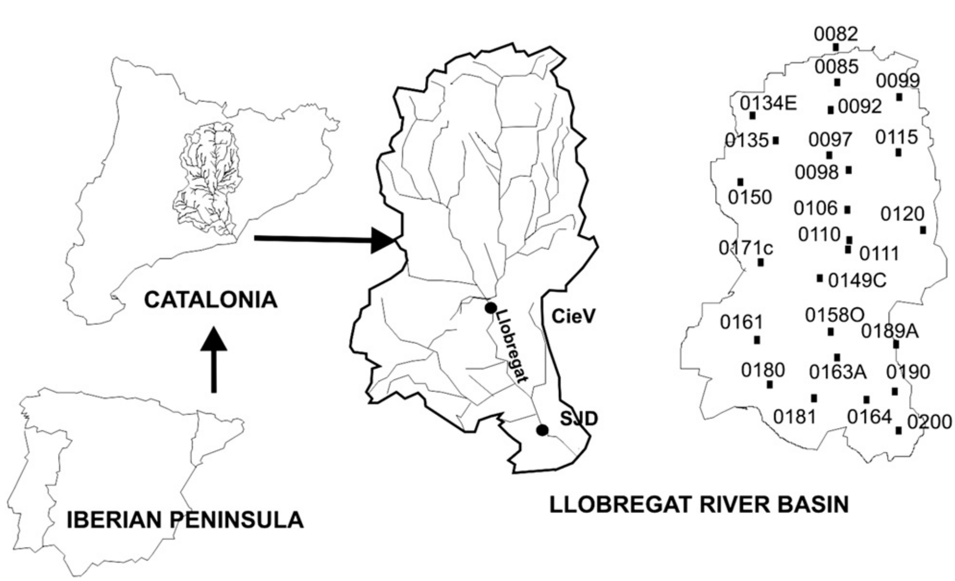


Fig. 1. Geographical location of the Llobregat basin (left) and water sampling stations (middle); distribution of the meteorological station within the basin (right).

El Niño during 1991–1995 and two consecutive La Niña years (1999 and 2000) without an intervening opposite phase.

Monthly nitrate z-scores were calculated as $z=(\mu-x)/\sigma$, were z is z-scores for nitrate values and z-scores > 1.96 indicate extreme nitrate concentrations, μ is the mean value for this month, x is the nitrate value at this month, and σ is the standard deviation for this month. With these z-scores, we compared precipitation anomalies series with extreme nitrate concentrations and Pearson Product Moment correlation coefficient to correlate both raw time series ($n=287$). We used the non-parametric Spearman's rank correlation coefficient (ρ) to measure the relationships SOI-scPDSI, SOI-nitrates and scPDSI-nitrates and tested its significance ($n<10$) (Zar, 1972). The correlations were calculated at a monthly basis (26 pairs of months for El Niño events, 12 pairs for La Niña events and 35 pairs for baseline conditions). Due to the time lag between the SOI signal and its effect on climatic variables in the Iberian Peninsula (Rodó et al., 1997; Vicente Serrano, 2005) correlations were computed considering a 0 to 12-month time lag between the ENSO signal and the remaining variables. Correlations between the scPDSI signal and nitrates were calculated under the same considerations. Seasons were defined as follows: winter (December–January–February), spring (March–April–May), summer (June–July–August) and autumn (September–October–November).

3. Results

Fig. 2 illustrates the nitrate series (a, b) and the nitrate extremes (c, d) in the Llobregat River at SJD and CieV. Average nitrate values

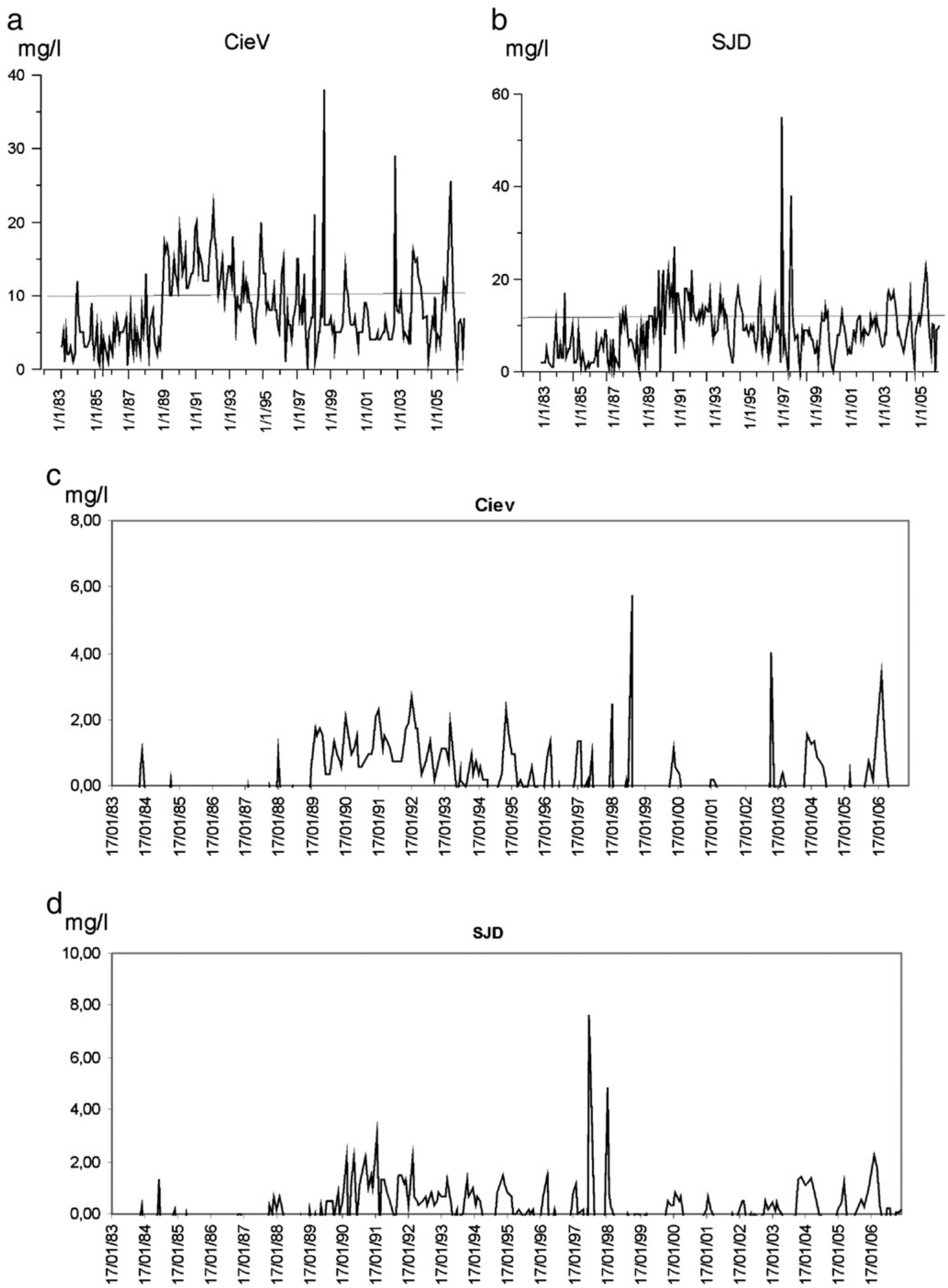


Fig. 2. Nitrate concentration time series (a, b). Y-axis: Annual nitrate concentration averages (mg/L). Nitrate extremes (c, d).

over the entire period were 8.1 ± 5.2 and 8.9 ± 6.0 mg/L, respectively. Correlation coefficient between both raw series was significant: r = 0.539 (ά = 0.005) and r = 0.334 (ά = 0.005), respectively. Weak peaking occurred between 1983/1984 (El Niño) and 1988/1989 (La Niña). The 1990s was an active ENSO decade (Trenberth and Hoar, 1996) and was marked by multiple nitrate peaks and higher nitrate minima than the years before and after. The largest nitrate peaks happened between 1997 and 1998 and coincided with the severe 1997/1998 El Niño event. High peaking also occurred during and immediately after 2002/2003 (El Niño). Most (78.2%) nitrate concentration extremes (z-scores > 1.96) occurred during ENSO or ensuing years (Fig. 2). Almost all intense daily precipitation events caused positive anomalies in the same month or the month before a nitrate extreme occurred (Fig. 3). Average monthly discharge values calculated for the period were $17.4 \pm 19.6\ m^3\ s^{-1}$ at CieV and $17.2 \pm 21.5\ m^3\ s^{-1}$ at SJD. Low correlations ($\rho < 0.4$) were found between monthly nitrate concentrations and monthly stream discharge series.

Furthermore, we investigated the correlations between precipitation at SJD and CieV and nitrates, between scPDSI and the SOI indices, between nitrate concentrations and the SOI indices, and between scPDSI and nitrate concentrations across the four climatic seasons of El Niño, La Niña, and neutral years. In the following sections we display the significant and most relevant results.

3.1. La Niña years

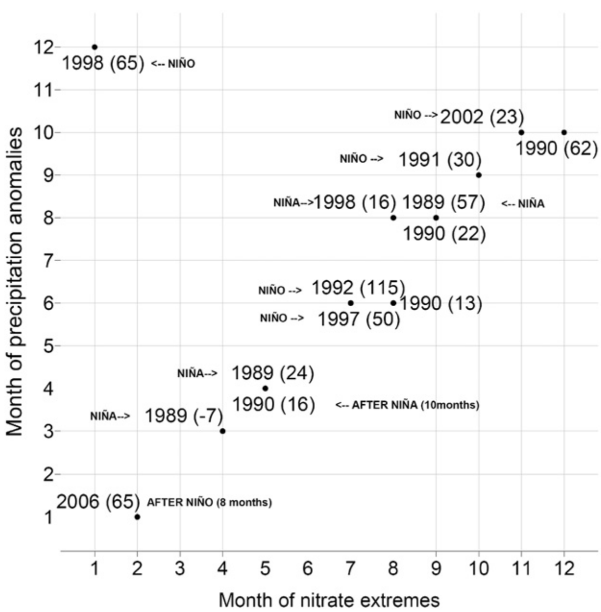
La Niña years showed the more significant correlations between the studied parameters. During spring (Fig. 4a,b) both stations display significant negative correlations between the spring SOI and scPDSI values (the more positive the SOI index, the more negative the scPDSI values) with 0- to 12-month delays, indicating that droughts started at spring and lasted until the spring of the following year. The spring SOI values at CieV were also correlated with nitrate concentrations (the more positive the SOI index, the higher the nitrate values), showing positive correlations with a time lag of 6–8 months (Fig. 4a), indicating that related nitrate increments occurred during the autumn/early winter. Similarly, spring SOI and nitrate concentrations at SJD showed a significant, but more delayed (8-months time lag) relationship (Fig. 4b).

During the summer of La Niña years, correlations were non-significant. During the autumn (Fig. 4c,d), SOI and scPDSI values had highly significant negative correlations, with a lag of 6–12 months, suggesting that the SOI did enhance drought conditions between spring and autumn of the ensuing year. Nitrate concentrations at CieV and SJD were first negatively correlated with the autumn SOI index, with a lag of 0–1 month (Fig. 4c) and 2–5 months (Fig. 4d), respectively, pointing to a decrease of nitrate concentrations with increasing SOI values during the same autumn (CieV) and the first (SJD) winter months. However, an inversion of the correlation sign took place in both cases, with 10–12 months and 8–12 months time lags at CieV and SJD, respectively, suggesting that positive increments in the SOI index would be related to increases in nitrate concentrations during the summer (CieV, SJD) and autumn (SJD) of the following year. During La Niña years, nitrate concentrations appeared to be negatively correlated with the scPDSI with 3 (Fig. 4c) and 4 months (Fig. 4d) time lags at CieV and SJD, respectively, indicating that nitrate concentrations may be responding to winter drought. During the winter of La Niña years (Fig. 4e), no significant correlations were found between the SOI and the scPDSI values at CieV. However, positive correlations were observed between winter SOI and nitrate concentrations with a 7–12 months time lags, suggesting that La Niña winter effects were promoting nitrate increases during the summer/autumn of the following year. Nitrate and scPDSI concentrations showed high negative correlations at CieV, with 0–5 months time lags, suggesting that winter drought caused increases in stream nitrate. No correlations were found at SJD.

On the other hand, nitrates and precipitation were correlated in summer and autumn only at CieV. During the summer, positive correlations occurred without delay ($\rho = 0.624$), suggesting that allochthonous nitrates were leached to the stream almost immediately by occasional summer storms.

3.2. El Niño years

During El Niño years, the relationships between the SOI, scPDSI, and nitrate concentrations at SJD and CieV were less clear (Fig. 4f–k). Correlations were not significant for SOI and scPDSI except in summer (Fig. 4f,g), and SOI and nitrate concentrations were positively but weakly correlated in every season. According to these patterns, more intense El Niño events (more negative summer SOI values) would promote more negative scPDSI values during the spring of the following year, and more intense El Niño events during spring, summer, and winter would reduce nitrate concentrations with a 10–12 months time lag (Fig. 4f,g). More negative SOI values during autumn seemed to be related to increase nitrate concentrations at both stations in the winter of the same year and in the spring of the following year (Fig. 4h,i). Summer and autumn were the only seasons showing significant positive correlations between scPDSI and nitrates (11–12 months time lag). On the other hand, significant positive correlations ($\rho = 0.350–0.628$) between precipitation and nitrates were found during the spring and the autumn seasons with 0–2 month time lags, indicating that the related nitrate increases took place within the same season (figures not shown).



NO3 extremes	April 1989	May 1989	September 1989	May 1990	August 1990	September 1990	December 1990
at CieV	**2.21**	**2.30**	**2.27**	**2.30**	0.58	1.73	**1.96**
at SJD	*-1.25*	*0.69*	*0.80*	***3.46***	***3.92***	***2.55***	*1.05*
Year	**October 1991**	**July 1992**	**July 1997**	**January 1998**	**August 1998**	**November 2002**	**February 2006**
at CieV	1.78	**2.46**	0.30	1.66	**4.04**	**3.11**	**2.72**
at SJD	***2.06***	*0.41*	***4.37***	***3.30***	*-1.70*	*0.46*	*1.78*

Fig. 3. Relationship between significant nitrate extremes and precipitation anomalies. The year of each event is indicated near each point and the monthly precipitation anomaly in mm is indicated in brackets. The table shows precipitation events occurred before the standardized nitrate anomalies (in bold z-value of nitrate > 1.96).

3.3. Neutral years

Neutral years showed low ($\rho<0.35$) but significant ($P=0.01$–0.05) correlations only between scPDSI and nitrates at CieV and SJD.

4. Discussion

4.1. La Niña versus El Niño years

Of the two ENSO phases and neutral years, the more evident relationship between droughts and the SOI occurred during La Niña years. The effect of La Niña upon the study area began in spring, once the SOI signal affected from the Pacific Basin through teleconnection mechanisms. Drier-than-usual conditions appeared and lasted throughout that year to the first months of the following year. Vicente Serrano (2005) obtained a similar result, showing year-long droughts during La Niña years for the northeast Iberian Peninsula using the standardized Precipitation Index (SPI). From the onset of SOI-drought in spring, higher-than-usual nitrates probably accumulated in the catchment soils due to reduced runoff, soil moisture, groundwater level and discharge. Later, high intensity autumn precipitation events of year x may have leached these nitrates, thus significantly contributing to river nitrate increments, as higher-than-usual allochthonous nitrate input could have taken place.

The autumn SOI of La Niña year further prolonged the ongoing drought conditions set by the spring SOI, to autumn of the following year, and coincided with a decrease in stream nitrate concentrations within the first month. A new combination of drought/catchment nitrate accumulation probably took place during this period, followed by precipitation/runoff events/leaching, increasing stream nitrate during summer and autumn of the next year (x)

The absence of a significant correlation linking the winter SOI and scPDSI at both SJD and CieV may be attributed to interactions of La

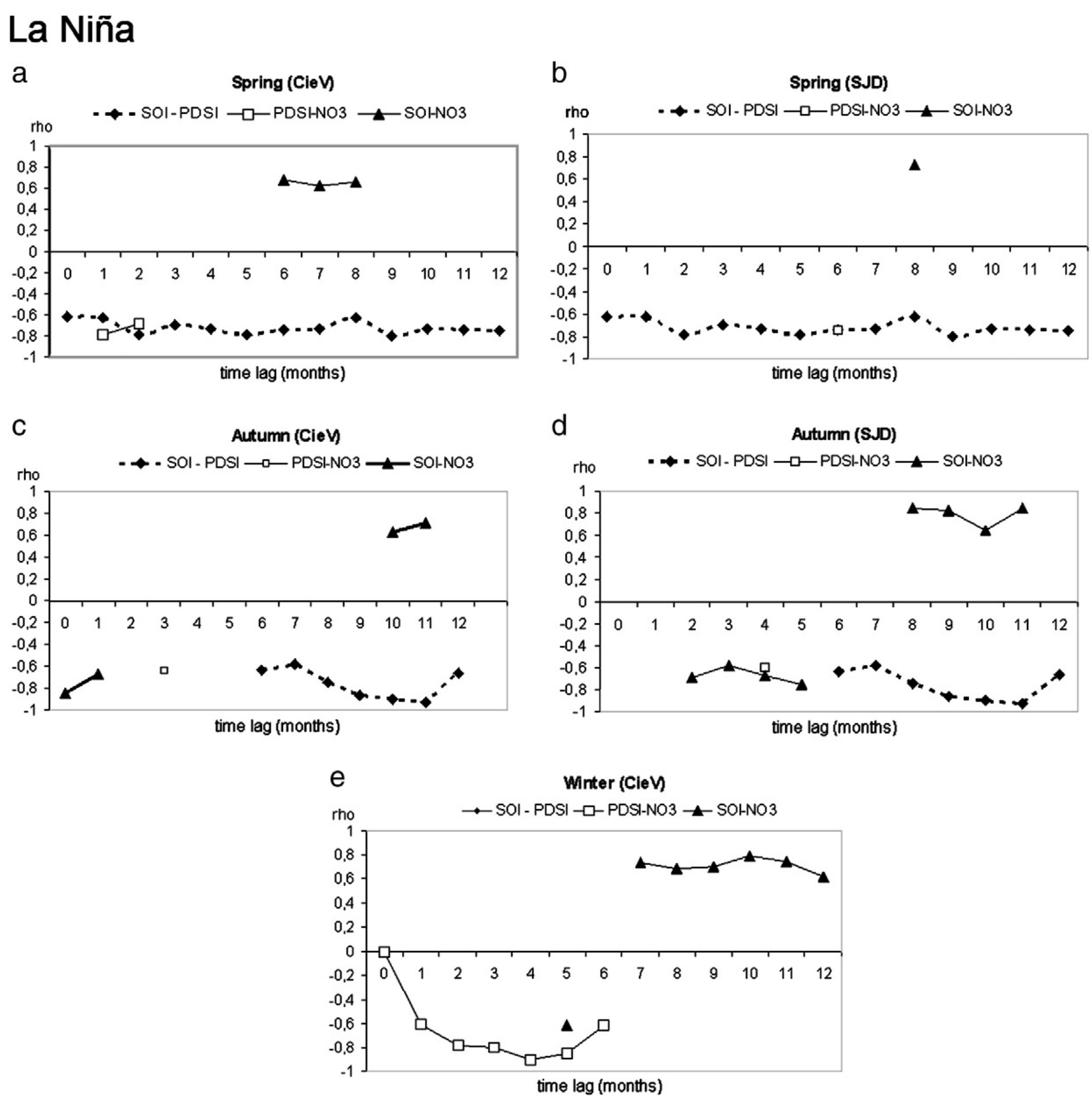


Fig. 4. Spearman's rho correlations between SOI and scPDSI, between SOI and nitrates, and between scPDSI and nitrates at CieV and SJD during La Niña (a–d) and El Niño (f–k) years. All correlation values were significant at the >90% levels. The graphs begin with month 0 (no time lag), which refers to the first month of the season (March, April or May) where the ENSO signal was detected. For example, the spring SOI signal can appear in March, April, or May, meaning that a drought or nitrate response with a time lag of 6 months would take place in September, October, or November, depending upon the starting month.

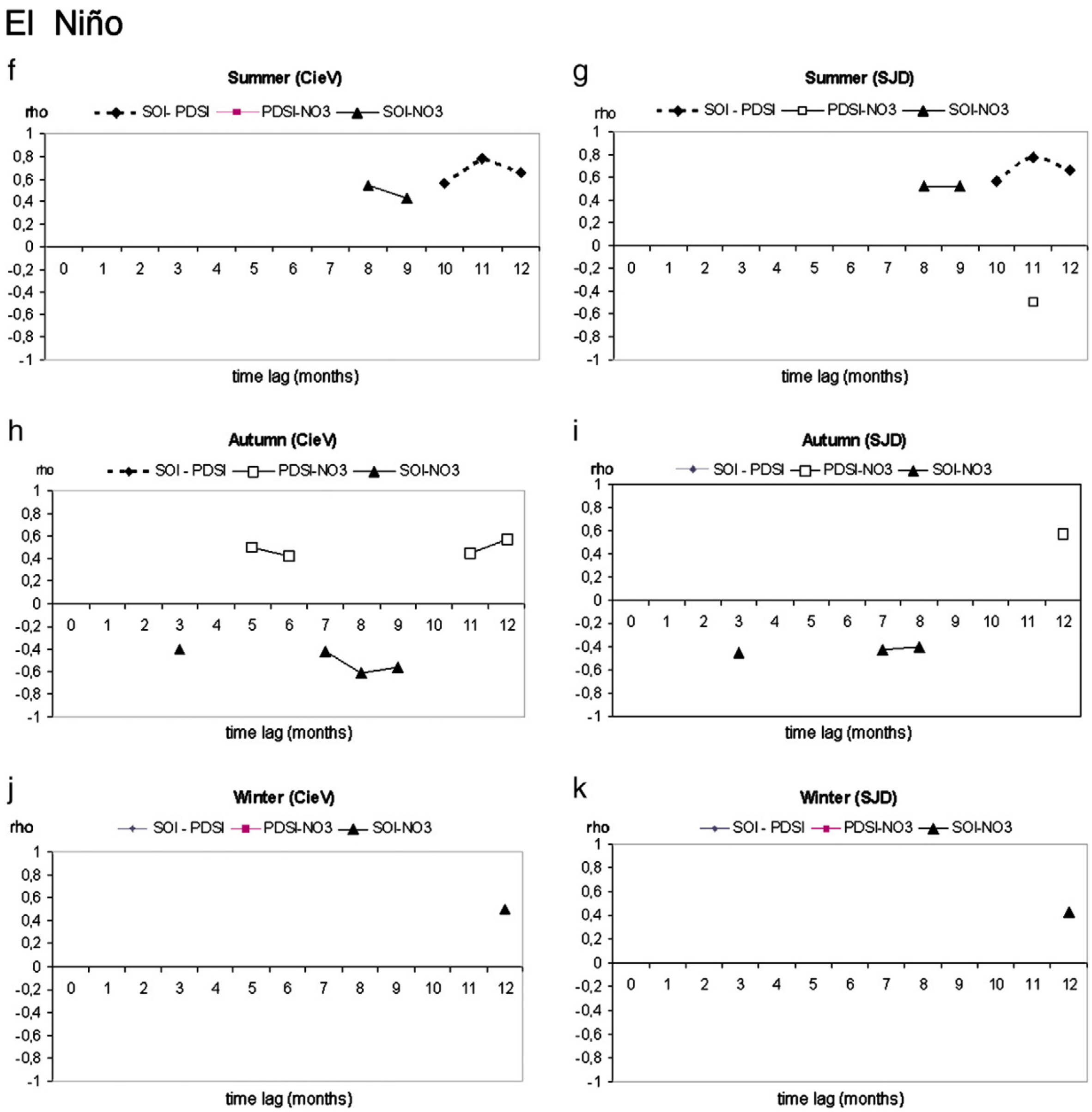


Fig. 4 (*continued*).

Niña signal with the biggest influence of the Atlantic circulation, the NAO, and the Pacific Decadal Oscillation (Zanchettin et al., 2008), which probably masked the expected SOI-scPDSI linkage. These interactions hamper the interpretation of the SOI-scPDSI-nitrate long-term trends in nitrate.

Our results do not show a clear pattern of nitrate concentrations for El Niño years. During El Niño years, the negative anomalies in the SPI were lower and less conspicuous than they were during La Niña years in the north-eastern Iberian Peninsula (Vicente Serrano, 2005), which may in part explain the lack of a statistical relationship between the SOI and scPDSI in the study area.

4.2. Hypothetical mechanisms triggering nitrate responses during La Niña years

Strong precipitation did not always trigger extreme nitrate responses, which commonly occurred during months with positive precipitation anomalies after a period of negative precipitation anomalies. This suggests that a condition for nitrate extremes is intense or above-average precipitation, after a period of severe hydric deficit. The summer and autumn contained most of the nitrate extremes and these seasons also included months of notable soil–water deficiency. Interestingly, under such low moisture conditions, nitrate response to increased precipitation was relatively fast (small delay). Similarly, some authors have found that the largest modifications in river nitrate concentrations were induced by storms following droughts (Àvila et al., 1992; Biron et al., 1999; Morecroft et al., 2000; Bernal et al., 2002). Flushing and groundwater displacement have been identified as responses to storm events (Iqbal, 2002). This suggests that during the prolonged precipitation shortage of La Niña years, nitrates (independently of their natural or anthropogenic origin) may accumulate in the near-surface zone of the basin. Nitrate peaks occurred only a few days after storms may reflect a rapid release of solutes from overland flow and near-surface soil layers associated with a rising water table (flushing), which occurs more quickly in dry soil. In contrast, months with delayed nitrate peaks may be attributed to a slower displacement of nitrate through groundwater into the stream (Iqbal, 2002).

5. Conclusion

1) The correlation analysis performed on a long time series (24 years) suggests that the ENSO, a disruption of the ocean–atmosphere system in the tropical Pacific Basin (Trenbergh, 1997) and the most prominent year-to-year climate variation of the Earth (McPhaden et al., 2006), may be influencing the temporal trends of dissolved nitrate in the Mediterranean Llobregat River, located thousands of kilometers away and outside the tropics, via atmospheric teleconnections.
2) The most affecting ENSO phase seems to be La Niña, whose influence begins in the spring after each ENSO year, as recorded in the core Pacific Basin using the SOI index. La Niña events promote year-long droughts, reducing runoff and edaphic moisture, and lowering groundwater levels and river discharge. Altogether, this may account for higher-than-usual nitrate storage in the catchment soils. This nitrate excess would be eventually transferred to the river by late-summer and fall precipitation and runoff thus causing the observed nitrate peaks.
3) The evidence presented here, combined with the results of other recent investigations in the Northern Hemisphere allow us to hypothesize that extreme nitrate concentration events in freshwater bodies may be affected by global or quasi-global teleconnection patterns among distant climatic systems.
4) Further research is necessary to elucidate the processes underlying the statistical correlations found in this study, and also to check whether the relationships found are reproducible in similar rivers, in order to make generalizations or not. The relative importance of natural climatic phenomena versus anthropogenic practices (as well as potential synergies between them) on river nitrate trends is also worth investigating. A proper understanding of the relationships between river nitrate concentrations, climate variables and regional low frequency atmospheric modes (ENSO, NAO, etc.), is crucial to predict long-term variability in the nitrate loadings of streams, and may be relevant at global biogeochemical scale. This knowledge would help to accurately establish correct environmental policies to preserve freshwater ecosystems at both short- and long-term.

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