

**Biogeochemical
characterization of
the riverine organic
matter**

M. Higuera et al.

Biogeochemical characterization of the riverine organic matter transferred to the NW Mediterranean Sea

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

A large amount of terrestrial organic matter is annually delivered by rivers to the continental shelf, where this material is either buried or transferred to the deep sea by hydrodynamic processes such as storms. The relative amount of terrestrial organic matter in the marine sediments is often determined by analyzing the stable isotopes ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) and the C/N ratio of organic matter because the various particulate organic matter (POM) sources have distinct isotopic compositions. With the objective to refine and better interpret POM sources in the marine environment, we have monthly characterized terrestrial POM delivered by eight rivers discharging to the NW Mediterranean Sea: Rhône, Hérault, Orb, Aude, Têt, Fluvià, Ter and Tordera rivers. These rivers were simultaneously sampled from November 2008 to December 2009 and the concentrations of total suspended matter (TSM), particulate organic carbon (POC) and nitrogen (PN), as well as their stable isotopic ratios ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) were determined.

During the survey, three rainstorm events with winds coming from the E–NE and the S–SE impacted the NW Mediterranean. Depending on the direction of incoming winds, the fluvial response (amount of water discharge and TSM) was different. Rivers draining the Alps (Rhône River) and Central Massif (Hérault, Orb, and Aude rivers) were mostly impacted by rainstorms associated with winds coming from the S–SE, while rivers draining the Pyrenees (Têt, Fluvià, and Ter rivers) and the Montseny Massif (Tordera River) were impacted by rainstorms associated with winds coming from the E–NE. In addition, the spatial evolution of water discharges shows different hydrological regime of the Rhône River, with relatively constant and high water stages and TSM concentrations when compared to coastal rivers, characterized by long periods of low water stages. TSM concentrations are positively correlated to water discharges (high water flows resuspended riverbed sediments) but show an inverse relationship with POC and PN relative contents (mostly due to dilution and by low availability of light in river waters during flood events). TSM in most of the coastal rivers have in average 2.5–3 times higher POC and PN mean contents than the Rhône River (8.5 %

BGD

10, 13277–13316, 2013

Biogeochemical characterization of the riverine organic matter

M. Higuera et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

and 1.5%, respectively for coastal rivers against 3.6% and 0.5%, respectively for the Rhône River). This discrepancy may be caused by the long drought periods in small coastal Mediterranean watersheds that enhance the eutrophication in studied coastal rivers. The $\delta^{13}\text{C}$ ratios of organic matter reflect also this discrepancy between high and low water stages with values ranging from -33.2‰ to -24.5‰ . The enriched ^{13}C values ($-26.3 \pm 0.4\text{‰}$ for the Rhône River and $-26.9 \pm 1.2\text{‰}$ for coastal rivers), measured during high water stages, express mostly a mixture of terrestrial source (plant remains and soils) whereas depleted ^{13}C values ($\sim -30\text{‰}$) associated with low water stages exhibit a source with predominant freshwater algae. The high $\delta^{15}\text{N}$ mean values ($> 8\text{‰}$) found in Têt, Ter and Tordera rivers underline the importance of denitrification processes as a consequence of the eutrophication and anthropogenic impact.

1 Introduction

Approximately 87% of Earth's land surface is connected to the ocean by rivers (Ludwig and Probst, 1998) which represent the primary pathway for water and particulate matter (mostly lithogenic particles and terrestrial organic matter) to the marine environment, contributing with $35\,000\text{ km}^3$ of freshwater (Milliman, 2001) and 18 GT yr^{-1} of suspended sediment (Milliman and Syvitski, 1992; Ludwig and Probst, 1998; Syvitski, 2003). These inputs are highly variable over time, shifting from low river discharges and low sediment inputs to the occurrence of flood events with high sediment supplies (Wheatcroft and Borgeld, 2000).

Numerous studies have documented the delivery of sediments to the ocean from large rivers such as the Amazon (e.g., Nittrouer and DeMaster, 1996), Yellow (Huanghe) (Liu et al., 2002, 2004), Ganges-Brahmaputra (Goodbred and Kuehl, 2000; Kuehl et al., 1997), and Yangtze (Changjiang) (Chen et al., 2001; Liu et al., 2007). However, Milliman and Syvitski (1992) emphasized the importance of smaller rivers ($< 5000\text{ km}^2$) and speculated that they may account for as much as half of the present-day sediment flux to the oceans.

BGD

10, 13277–13316, 2013

Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Biogeochemical
characterization of
the riverine organic
matter**

M. Higueras et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

River inputs play a major role in the semi-enclosed Mediterranean Sea, because changes in their inputs are therefore potential drivers for long-term changes in the marine ecosystems (Ludwig et al., 2009). Recent studies have shown that freshwater discharges by Mediterranean rivers decreased significantly from about 20 % between 1960 and 2000 (Ludwig et al., 2009). This reduction is probably the result of several stress factors including climate change and dam construction (Ludwig et al., 2003). First, the increase of temperature during the 20th century, in particular since the late 1970's (Gulf of Lion: $0.5\text{ }^{\circ}\text{Cdecade}^{-1}$ for 1979–2004; Lespinas et al., 2010) and the decrease of precipitation during certain periods of the year in the upstream watersheds may cause a significant water discharge reduction (López-Moreno et al., 2008; Lespinas et al., 2010). Second, rivers are highly affected by the artificial river damming often related to water extractions for irrigation (Ludwig et al., 2003) which alter the natural functioning of Mediterranean rivers. The Nile River is a clear evidence of this, with a decrease from 40–45 to 15 km^3 of freshwater discharge to the Mediterranean Sea after building the Aswan High Dam in 1964 (Schroeder et al., 2012).

At present, the Rhône River represents the major source of freshwater and terrestrial particulate matter to the Mediterranean Sea (Margat, 1992; Pettine et al., 1998; Sempéré et al., 2000). Furthermore, the Mediterranean shore is characterized by numerous coastal rivers that discharge significant amounts of water and sediment during the occurrence of short but violent flash flood events (Serrat et al., 2001; Bourrin et al., 2008). Several studies carried in the NW Mediterranean Sea have shown that terrestrial sediments including particulate organic matter (POM) are deposited on the continental shelf, which act as transit zone between land and deep basins. Besides accumulation, physical processes (i.e. dense shelf water cascading induced by cold winds and downwelling induced by eastern storms) occurring at the shelf edge are capable of transferring matter to the deep sea (Palanques et al., 2006; Sanchez-Vidal et al., 2009, 2012). Therefore, it is essential to accurately assess the origin and nature of the organic matter discharged by Mediterranean rivers to the continental shelf for

understanding the carbon and nitrogen cycling not only in the shallow but also in the deep marine environment.

Riverine organic matter derives from two fundamentally different sources, which are autochthonous aquatic production and allochthonous plant detritus deposited on the ground (Finlay and Kendall, 2007). Stable isotopes offer an important tool for estimating the relative contributions of both autochthonous and allochthonous sources of terrestrial POM. Indeed carbon and nitrogen isotopic ratios ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) are widely used as natural tracers of carbon sources in estuarine and marine coastal ecosystems (Riera and Richard, 1997; Rolff and Elmgren 2000; Darnaude et al., 2004; Wissel and Fry, 2005). In the NW Mediterranean, several studies on the Rhône River (Aucour et al., 2003; Darnaude et al., 2004; Harmelin-Vivien et al., 2010) have been carried out to determine the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signatures of total suspended matter (TSM). In the TSM of the Rhône River, the $\delta^{13}\text{C}$ mean ratios have been set at -27.4‰ in 1996 and -26.1‰ in 2001 (Aucour et al., 2003, and Darnaude et al., 2004), -26.6‰ in 2004 and -27.4‰ in 2005 (Harmelin-Vivien et al., 2010). $\delta^{15}\text{N}$ ratios have been scarcely measured and only mean values of 5.7‰ and 4.8‰ in 2004 and 2005, respectively, have been published by Harmelin-Vivien et al. (2010). Recently, the suspended matter in the coastal rivers Fluvià, Ter and Tordera has been isotopically characterized (Sanchez-Vidal et al., 2013). The $\delta^{13}\text{C}$ mean values found are quite similar to the Rhône River with -28.6 , -27.3 and -28.1‰ at the Fluvià, Ter and Tordera rivers, respectively. Moreover, these coastal rivers exhibited higher $\delta^{15}\text{N}$ mean values ranging from 8.5 to 10.4‰ . Overall, these results show that suspended POM in NW Mediterranean rivers is a mixture of terrestrial (plant remains and soils) and algae (freshwater phytoplankton) organic matter sources.

Up to date, few coastal Mediterranean rivers have been studied and no investigations have been carried out to trace simultaneously the POM discharged by all the small and large rivers flowing into the NW Mediterranean Sea. The main objective of this work is to accurately assess the quantity and quality of POM discharged into the NW Mediterranean Sea by the eight main rivers (from north to south: Rhône, Hérault, Orb,

BGD

10, 13277–13316, 2013

Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Aude, Têt, Fluvià, Ter and Tordera) and investigate their role in the transport of POM according to their watersheds and anthropogenic uses, as well as the occurrence of meteorological events. This study will help us to determine the spatial and temporal variations of the riverine inputs (TSM, particulate organic carbon (POC) and nitrogen (PN)) into NW Mediterranean Sea and POM sources and determine their relation to water flows.

2 Material and methods

2.1 Study area

This study is focused on eight rivers discharging into the NW Mediterranean Sea (Fig. 1), which is characterized by warm temperatures, winter-dominated rainfall, dry summers and a profusion of microclimates due to local environmental conditions (Ludwig et al., 2003). The most important river is the Rhône River, with the largest catchment in Western Europe (97 800 km²), and the highest freshwater input to the Mediterranean Sea (mean annual discharge of 1710 m³ s⁻¹ for the period 1961–1996). The Rhône River originates in the Alps Mountains (Switzerland) at an elevation of 2150 m, follows a course of 812 km and meets the sea at the Camargue Delta (south-eastern France). Near its mouth, at 40 km from the sea, the river splits into two distributaries, so-called the Great Rhône and Little Rhône, carrying about 90 and 10% of the water discharge, respectively (Ibañez et al., 1997).

We report also on seven coastal Mediterranean rivers that flow into the NW Mediterranean Sea with draining catchment areas lower than 5000 km² which are the Hérault, Orb, Aude, Têt, Fluvià, Ter and Tordera rivers. In contrast to the Rhône River, their water discharges are torrential in their character, and water discharges are low during long periods except in times of heavy rainfall that causes flash floods (Paloc, 1967). Moreover, these rivers are also characterized by high percentage of vegetated land and

BGD

10, 13277–13316, 2013

Biogeochemical characterization of the riverine organic matter

M. Higuera et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

may be highly affected by anthropogenic activities in their downstream parts (Lespinas et al., 2010).

The Hérault River originates in the Cévennes Mountains (Central Massif). The river is 150 km long and drains a medium-size basin of 2500 km² with a mean annual discharge of 44 m³s⁻¹. The basin comprises very few industries and is predominantly dedicated to agriculture. It can be considered as a relatively rural watershed.

The Orb River rises in the Central Massif at an elevation of 820 m. This river follows a course of 136 km, and drains an area of approximately 1800 km² with a mean annual discharge of 25 m³s⁻¹. The middle part and the alluvial plain of the watershed is characterized by agricultural activities.

The Aude River originates in the Pyrenees, follows a south–north course to Carcassonne before turning abruptly towards the east to enter the Mediterranean. This river is the longest of the investigated coastal rivers (224 km) and its watershed covers an area of 4840 km² with a mean annual discharge of 49 m³s⁻¹. The Aude River plain, the tributary valleys and the moderate slopes are mainly covered by vineyards (Gaume et al., 2004).

The Têt River drains an area of 1400 km² on the eastern part of the Pyrenees. The river follows a course of 120 km with a mean annual discharge of 7.5 m³s⁻¹. The agricultural activities from the plain and the urban waste-waters from Perpignan's district (about 150 000 inhabitants) have a great influence on the chemistry of the Têt River (Garcia-Esteves et al., 2007).

The Fluvià River originates in the Pre-Pyrenees at an elevation of 920 m and is the only of all the studied rivers that remains undammed along its entire course. This river follows a course of 97.2 km and drains an area of approximately 1125 km² with a mean annual discharge of 9 m³s⁻¹. The Fluvià watershed, as well as the watersheds of Ter and Tordera rivers are quite densely vegetated, mostly by gramineae with woody elements and by coniferous forests, which cover around 50% of the Fluvià, Ter and Tordera watersheds (Liquete et al., 2009).

**Biogeochemical
characterization of
the riverine organic
matter**

M. Higueras et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Biogeochemical
characterization of
the riverine organic
matter**

M. Higuera et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The Ter River rises in the southeastern part of the Pyrenees at an elevation of 2400 m and follows a course of 208 km with a mean annual discharge of $12 \text{ m}^3 \text{ s}^{-1}$. Its watershed covers an area of 3010 km^2 and is regulated by dams (97 % of the watershed area) (Liquete et al., 2009). The reservoirs of Sau, Susqueda and Pasteral are located in the middle course. Damming impact on the physical-chemical and biological characteristics of the lower stretch of the river is notable (Sabater and Armengol, 1986).

The Tordera River originates in the Montseny Massif (Fig. 1) at an elevation of 1712 m, follows a course of 60 km with a mean annual discharge of $7 \text{ m}^3 \text{ s}^{-1}$ and drains an area of 894 km^2 .

2.2 Sampling strategy

The Rhône, Hérault, Orb, Aude, Têt, Fluvià, Ter and Tordera rivers were monthly and simultaneously sampled from November 2008 to December 2009. Sampling stations were located on the lower most course of each river in order to collect the particulate material that will be discharged into the sea. Water samples of Rhône and Têt rivers were collected from two automatic sampling stations (Arles and Villelongue-de-la-Salanque, respectively) whereas Hérault, Orb and Aude rivers were sampled from bridges at the middle of the river banks. Fluvià, Ter and Tordera rivers were sampled from the shore near the last gauging station of the *Agència Catalana de l'Aigua*. Twenty liters of water were collected on each river and stored in polyethylene bottles in a refrigerated room (5°C) in darkness.

2.3 Analytical method

The collected water was filtered onto pre-combusted (at 450°C for 12 h) Glass-Fibre Filters (GF/F). Then, filters were freeze-dried, weighted for determining the concentration of TSM and stored in desiccators before analysis.

Prior to the POC analysis, the inorganic carbon (mainly in the form of calcium carbonate) was removed by repeated additions of $100 \mu\text{L}$ of HCl 25 % separated by 60°C

Biogeochemical characterization of the riverine organic matter

M. Higuera et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

drying steps until no effervescence was noticed (Fabr es et al., 2002). Then, POC and PN contents from the Rh one, H erault, Orb, Aude and T et rivers were measured on a Leco CN 2000 elemental analyzer and stable isotopic ratios ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) with an Isotopic Ratio/Mass Spectrometer (IR/MS, GVI Isoprime) at CEFREM laboratory.

POC and PN contents from the Fluvi a, Ter and Tordera rivers were analysed on an Elemental Analyzer interfaced to an IR/MS (Delta Plus Finnigan MAT, and interface GC Combustion III Finnigan MAT) at the Scientific-Technical Services of the University of Barcelona. POC and PN are expressed in % of the sample dry weight and isotopic ratios are given in the conventional δ notation:

$$\delta^{13}\text{C} \text{ or } \delta^{15}\text{N} = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \right] \times 1000$$

where R corresponds to $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$ and the reference materials are the international standards Pee Dee Belemnite (PDB) and atmospheric N_2 for C and N, respectively. The standard deviations from $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ replicates of internal standards were lower than 0.2‰ at CEFREM laboratory and 0.2‰ and 0.3‰, respectively, at the Scientific-Technical Services of the University of Barcelona.

A PCA (principal component analysis) was carried out using the SPAD (Specification Planning Architecture & Design) software (SPAD, 2000). Each field sample was considered as a statistical individual characterized by 6 numeric active variables (TSM, Q (water discharge), POC, PN, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$) and by 3 categorical variables (month, river and water discharge coded in two modalities: low and high) that were integrated in the analysis as supplementary variables.

The variables were considered as statistically significant when the absolute value of test values was larger than 2 (Lebart et al., 1984).

3 Results

The mean water discharge (Q) of the Rh one River was of $1386 \text{ m}^3 \text{ s}^{-1}$, which was much larger than those recorded in the coastal rivers ($3\text{--}38 \text{ m}^3 \text{ s}^{-1}$) (Table 1). All mean water

**Biogeochemical
characterization of
the riverine organic
matter**

M. Higuera et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

flows calculated during the survey period were lower than long-term (40 yr) averaged values (see Sect. 2.1) so the studied period can be considered as dryer than usual. Time series of water discharge show a strong variation in the coastal rivers (Fig. 2). Indeed, high and punctual (a few days long) water flows were recorded in November 2008, December 2008 and February 2009, whereas a wider (a few weeks long) high water stage occurred in April–May 2009. In contrast, extremely low water flows were recorded during long periods (from July to October 2009). The water discharge of the Rhône River was higher and relatively constant during the survey period in spite of flow peaks occurring also in November 2008, December 2008 and February 2009.

TSM concentrations in the Rhône River ranged from 5.5 to 488.7 mgL⁻¹, with a mean of 71.9 mgL⁻¹, whereas in the coastal rivers TSM ranged from 0.5 to 223.1 mgL⁻¹ with a mean of 15.9 mgL⁻¹ (Table 1). Indeed, in the coastal rivers a high TSM concentration was measured in November 2008 (57.1, 22.2 and 194.7 mgL⁻¹ in Hérault, Orb and Aude rivers, respectively), February 2009 (86.5, 27.5 and 103.4 mgL⁻¹ in Fluvià, Ter and Tordera, respectively) and April–May 2009 (223.1 and 28.4 mgL⁻¹ Têt and Ter rivers) coinciding with an fast increase of water discharge (Fig. 2). Unfortunately, TSM were not sampled over the highest *Q* recorded in December 2008 by Têt, Fluvià, Ter and Tordera rivers and in February 2009 by Hérault, Orb and Aude rivers. Moreover, Rhône River measured a relatively constant TSM concentration during the studied period except in November 2008 and February 2009 where the highest TSM concentration (330.6 mgL⁻¹ and 488.7 mgL⁻¹, respectively) were measured coinciding with the highest *Q* recorded during the survey (Fig. 2).

The contribution of POC to TSM (expressed as percentage) ranged from 1.2 (March 2009) to 6.7 % (August 2009) in the Rhône River (mean of 3.6 %), and from 1.1 % (November 2008 in the Aude River) to 23.5 % (June 2009 in the Tordera River) in the coastal rivers (mean of 7.1 %). PN percentages ranged from 0.1 (February 2009) to 1.1 % (October 2009) in the Rhône River (mean of 0.5 %), and from 0.2 % (November 2008 in the Aude River) to 4.6 % (September 2009 in the Tordera River) in the coastal rivers (mean of 1.5 %) (Table 1). Coastal rivers recorded the lowest POC and

**Biogeochemical
characterization of
the riverine organic
matter**

M. Higuera et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

PN contents in November 2008 (POC: 2.7, 4.5 and 1.1 % and PN: 0.3, 0.6 and 0.2 % in Hérault, Orb and Aude rivers, respectively), February 2009 (POC: 5.7, 5.8 and 3.8 % and PN: 0.9, 0.7 and 0.4 % in Fluvià, Ter and Tordera, respectively) and April–May 2009 (POC: 3.7 % and PN: 0.9 % in Têt River) which coincide with peaks of the water discharge (Fig. 3). Comparatively, the Rhône River measured low and relatively constant POC and PN contents during the studied period. The lowest POC and PN contents (1.25 % and 0.14 %, respectively) were measured during the highest Q recorded in February 2009 (Fig. 3).

Stable isotopic ratios of suspended organic matter from rivers varied from -33.2‰ to -24.5‰ for $\delta^{13}\text{C}$ and from 1.93‰ to 16.8‰ for $\delta^{15}\text{N}$ (Table 1). The $\delta^{13}\text{C}$ values were high ($> -27\text{‰}$) and relatively constant (standard deviation $< \pm 1\text{‰}$) in the Rhône, Orb, Têt and Ter rivers. In contrast, values were lower ($< -28\text{‰}$) and more variable (standard deviation $> \pm 1.5\text{‰}$) in the Hérault, Aude, Fluvià and Tordera rivers (Fig. 4). The $\delta^{15}\text{N}$ values were low ($< 6\text{‰}$) and relatively constant (standard deviation around $\pm 1\text{‰}$) during the survey in the Rhône, Orb and Hérault rivers. The Aude River showed also relatively low but more variable values. In contrast, high ($> 7\text{‰}$) and dispersed values (standard deviation $> \pm 2\text{‰}$) were recorded in the Têt, Ter and Tordera rivers. The Fluvià River exhibited also high but almost constant $\delta^{15}\text{N}$ values (standard deviation around $\pm 1\text{‰}$) (Fig. 4).

The atomic C/N ratios of particulate organic matter varied over a large range from 2.8 to 14.7 (Table 1). The lowest values (< 3) were obtained in the Orb and Tordera rivers in June and September 2009. On the other hand, Rhône, Ter and Tordera rivers recorded the highest values (> 12) in November 2008, February and July 2009.

The first two factorial axes of the PCA accounted for 66.16 % of the total variability (47.71 % for axis 1 and 18.45 % for axis 2, Fig. 5). The first component opposed a group of 3 active variables (POC, PN and $\delta^{15}\text{N}$) and 4 categorical variables (October 2009, Fluvià, Tordera, Low Flow) of positive coordinates to an another group of 3 active variables (Q , TSM and $\delta^{13}\text{C}$) and 4 categorical variables (February 2009, November 2008, Rhône and High Flow) of negative coordinates. The second compo-

ment opposed a group of 4 active variables (Q , TSM, POC and PN) and one categorical variable (Rhône) of positive coordinates to one active variable ($\delta^{13}\text{C}$) and 1 categorical variable (January 2009) of negative coordinates. The variable $\delta^{15}\text{N}$ was not significantly correlated with the second component.

4 Discussion

4.1 Meteorological and hydrological drivers of terrestrial organic matter input to the NW Mediterranean

From a meteorological point of view, the NW Mediterranean Sea is mainly affected by N–NW, E–NE and S–SE winds. Heavy winds coming from E–NE (90 to 45°) and S–SE (180 to 135°) are warm and loaded with moisture, and when meet the cold air aloft the Massif Central relief and the Pyrenees mountains the atmosphere becomes unstable and rain falls over these mountains. These types of rainstorms are named *Cévenol* when caused by S–SE winds (more frequent in the northern Gulf of Lions due to the orientation of the coast, see Fig. 1), and *Llevantada* when caused by E–NE winds (more frequent in the Catalan Coast). This causes sudden and elevated river discharges that can last for a few hours to days, the so called flash flood events.

During the studied period (from November 2008 to December 2009), three rainstorm events with E–NE and S–SE wind directions impacted the study area and affected differently rivers discharging to the NW Mediterranean Sea (Fig. 2).

The first event was recorded on the 3rd November 2008 following a two months-long dry period. This rainstorm was associated with a mean wind direction from 170° (recorded at the meteorological station of Cap Béar) and caused an increase of water flows in rivers from the Alps (Rhône River) and Central Massif (Hérault, Orb, and Aude rivers). Indeed the Aude River, although originating in the Pyrenees, is influenced by tributaries coming from the Central Massif. The highest Q values were recorded in the Rhône River (up to $4806 \text{ m}^3 \text{ s}^{-1}$) with a calculated return period of 2 yr, followed by the

BGD

10, 13277–13316, 2013

Biogeochemical characterization of the riverine organic matter

M. Higuera et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Hérault River ($455 \text{ m}^3 \text{ s}^{-1}$, return period of 1 yr). Lower values were recorded in rivers of Pyrenees and Montseny Massif (Têt, Fluvià, Ter and Tordera), with Q values around $20 \text{ m}^3 \text{ s}^{-1}$.

On the 26th December 2008 a severe rainstorm impacted the Catalan coast (Sanchez-Vidal et al., 2012). Heavy winds blowing from E–NE (the mean wind direction recorded at the meteorological station of Cap Béar was of 90°) triggered rainfalls especially in the Pyrenees and the Montseny Massif. On the 27 and 28 December rivers originating from these mountains reached their highest Q of the studied period (up to $155.9 \text{ m}^3 \text{ s}^{-1}$), with return periods of 1 to 3 yr (Fig. 2).

The third rainstorm event occurred in early February 2009. Heavy S–SE winds (the mean wind direction recorded at the meteorological station of Cap Béar was of 170°) triggered intense rainfall in the Central Massif and, thus, increased Q values up to $4848 \text{ m}^3 \text{ s}^{-1}$ in the Rhône and up to 687 and $280 \text{ m}^3 \text{ s}^{-1}$ in the northern most coastal rivers (Hérault and Orb rivers, respectively) (Fig. 2). This corresponded to a return period of 1.5–2 yr.

The direction of the incoming wind produced different hydrological responses of the investigated rivers. Windstorms from the E–NE caused increased water discharge in rivers from Pyrenees (Têt, Fluvià, Ter rivers) and Montseny Massif (Tordera River) whereas windstorms from the S–SE caused increased flows of rivers from the Alps (Rhône River) and Central Massif (Hérault, Orb, Aude rivers). In addition, some of the coastal rivers (Hérault, Orb, Aude, Têt and Ter) recorded simultaneously a significant increase of water discharges in April–May 2009. Increased insolation in spring caused snowmelt that impacted the rivers flowing from the mountains that accumulate large amounts of snow during the winter season (mostly the Massif Central and the Pyrenees).

Therefore, rainstorms and snowmelt were the major mechanisms triggering increased water flows that may increase sediment inputs to nearshore waters of the NW Mediterranean Sea. It is well-known that fast increases of Q associated with heavy rainstorms cause the erosion of the riverbanks and the resuspension of riverbed sed-

BGD

10, 13277–13316, 2013

Biogeochemical characterization of the riverine organic matter

M. Higuera et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Biogeochemical characterization of the riverine organic matter

M. Higuera et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

iments, removing the sediments accumulated during low water flow periods (Liquete, 2008). In order to elucidate the relationship between water discharges and TSM a sediment rating curve was established. The most commonly used is a power function with the standard form $TSM = a \cdot Q^b$, where a and b are regression coefficients (Asselman, 2000). The sediment rating curve shows a good correlation between log TSM and log Q in the Rhône River ($R^2 = 0.8$) (Fig. 6), and relatively poorer in coastal rivers ($0.3 < R^2 < 0.7$) (Fig. 6). It should be noted that Orb and Aude rivers don't have any correlation between Q and TSM, as it was found by Liquete et al. (2009) in several coastal rivers flowing into the Catalan margin. Therefore, the use of sediment rating curve to estimate TSM in the Rhône River is relatively accurate, whereas caution is needed for the coastal rivers. This is probably caused by two main factors. First, the strong natural temporal variability of the water flow. Brooks et al. (2003) reported that the rivers with flash flood events may take years to recover its original sediment curve. Second, the high impact of anthropogenic activities, such as dam constructions and water extractions for irrigation, that are very efficient filters for particulate matter (Meybeck and Vörösmarty, 2005), may alter the natural functioning of coastal rivers in term of sediment transport (Liquete, 2008; Ludwig et al., 2009). In many fluvial systems has been documented the impact of dam constructions, which intercept half of the water discharge, store at least 30 % of sediment fluxes (in major fluvial systems) and produce variations in the composition of suspended material (Meybeck and Vörösmarty, 2005; Syvitski et al., 2005). On the other hand, fluvial systems affected by irrigation, sometimes associated with water diversion from one basin to another, have much lower transport potential than under natural conditions (Meybeck and Vörösmarty, 2005).

The mechanism that controls the export of riverine POM is the riverine sediment load (Meybeck, 1982; Ludwig et al., 1996). The POC and PN contents of the TSM (in percentage) are usually highly variable in world rivers, ranging from 0.3 to 37 % (Ittekkot and Arain, 1986; Cauwet et al., 1990; Martin-Mousset et al., 1997) and from 0.1 to 1.3 % (Malcolm and Durum, 1976; Meybeck, 1982), respectively. In this study a wide range has been also found (from 1.1 to 23.5 % of POC and 0.1 to 4.6 % of PN). In order

to prove the relationship between %POC and TSM and %PN and TSM in studied rivers the power functions %POC and %PN = $a \cdot TSM^b$ have been also established.

The inverse relationship between %POC and TSM and %PN and TSM obtained in most of sampled rivers (Figs. 7 and 8) suggests dilution of the riverine POC and PN by the mineral matter resuspended from the riverbed during flash flood events. When the intensity of rainfall exceeds the infiltration rate, the soil surface becomes saturated in water and the eroded surface material is carried into streams and rivers. In Mediterranean coastal watersheds, the long dry periods between rainfall events reduce the infiltration rate and emphasized the soil erosion (Nadeu et al., 2012). In addition, during events of high Q and TSM the in situ primary production of POC and PN by riverine phytoplankton may be reduced because of the high turbidity and the low availability of light in river waters (Ludwig et al., 1996; Ni et al., 2008).

In contrast, the suspended material of coastal rivers was enriched in POC (from 9.3 to 23.5 %) and PN (from 1.6 to 4.6 %) during low water stages when TSM concentrations were low ($< 5.4 \text{ mg L}^{-1}$). In this case photosynthesis can be an important contributor to POC and PN in low turbidity waters (Ni et al., 2008). The calm and stagnant waters in coastal rivers, associated with high water temperature may favor the proliferation of freshwater phytoplankton. In the Rhône River, the low water stages do not produce stagnant waters that enhance the primary production as in coastal rivers and, moreover, the mean TSM content is about 5 times higher than in coastal rivers. This high turbidity attenuates the photosynthetically available radiation (PAR) by producing a “shadow” effect. Harmelin-Vivien et al. (2010) found that the autochthonous phytoplankton in the downstream part of the Rhône River accounted in average for only 10 % of the POM. For that reason, suspended particles of coastal rivers seem to be particularly more enriched in POM than the Rhône River (Table 1, Figs. 6 and 7).

Besides having a critical effect over the suspended sediment transport, river damming may be also the responsible of the poor relationship between %POC and TSM and %PN and TSM in the Orb and Ter rivers (Figs. 6 and 7). Therefore, trapping

BGD

10, 13277–13316, 2013

Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

of sediments by dams may also cause a decrease of POC and PN transport from the terrestrial to the marine environments (Sanchez-Vidal et al., 2013).

The amounts of TSM and POC delivered annually (2008–2009) to the NW Mediterranean Sea by the studied rivers have been estimated using the above mentioned power functions and the daily Q data (Table 2). We found that the Rhône River delivered $2.8 \cdot 10^6 \text{ tyr}^{-1}$ of TSM and $5.8 \cdot 10^4 \text{ tyr}^{-1}$ of POC, while the sum of the studied coastal rivers discharged $0.1 \cdot 10^6 \text{ tyr}^{-1}$ of TSM and $0.6 \cdot 10^4 \text{ tyr}^{-1}$ of POC. Thus, coastal rivers accounted for approximately 5 % and 10 % of the Rhône River fluxes (TSM and POC, respectively). Our estimations for the Rhône River match those found by Cauwet et al. (1990) for the period 1986–1987 ($2.8 \times 10^6 \text{ tTSMyr}^{-1}$ and $7.9 \times 10^4 \text{ tPOCyr}^{-1}$).

It is important to notice that both studies were carried out during dry periods as our Q means were lower than the long-term mean of the Rhone River ($1710 \text{ m}^3 \text{ s}^{-1}$). In contrast, Sempéré et al. (2000) reported for 1987–1996 higher TSM and POC fluxes ($9.9 \times 10^6 \text{ tyr}^{-1}$ and $19.2 \times 10^4 \text{ tyr}^{-1}$, respectively) than in this study. During this 10 yr survey more than 15 flood events over $5000 \text{ m}^3 \text{ s}^{-1}$ were recorded, whereas no similar peaks have been found during years 2008–2009 and since December 2003. Comparisons can also be done on the most studied of the coastal rivers, the Têt River. Our annual TSM and POC flux estimations (8339 tTSMyr^{-1} and 393 tPOCyr^{-1}) exhibits significantly lower fluxes than fluxes ($16\,046 \text{ tTSMyr}^{-1}$ and 524 tPOCyr^{-1}) reported for the period 2000–2001 (Garcia-Esteves, 2005) and than TSM fluxes ($50\,000 \text{ tyr}^{-1}$) calculated for the 1980–1999 period (Serrat et al., 2001). These latter authors revealed an extreme variability between annual water and sediment fluxes. According to Serrat et al. (2001), more than 50 % of the overall sediment transported for the 20 yr of investigation was discharged during only 13 days. It becomes evident that estimates of TSM and POC fluxes from coastal rivers depend on whether the survey has been performed during dry, normal or humid years.

**Biogeochemical
characterization of
the riverine organic
matter**

M. Higuera et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4.2 Sources of POM transferred to the NW Mediterranean Sea

Riverine POM is habitually composed of a mixture of organic matter derived from autochthonous aquatic production and allochthonous terrestrial detritus of various origins (Maksymowska et al., 2000; Finlay and Kendall, 2007; Harmelin-Vivien et al., 2010) which include vascular plants, soil-derived organic matter and freshwater algae. The proportions of each source may vary according to the size of watershed, meteorological factors such as the occurrence of storms and the presence of anthropogenic inputs. In the Mediterranean basins the natural forest and grassland are dominated by C3 plants (mainly higher plants), although a minor contribution of invasive C4 plants (cactus and herbs) are found in some areas of the Mediterranean coast (Sage et al., 1999; Novara et al., 2011). C3 plants are characterized by $\delta^{13}\text{C}$ values from -25‰ to -28‰ (Hedges et al., 1997), $\delta^{15}\text{N}$ values from 3‰ to 7‰ (Ongri et al., 2008) and C/N values from 20 to 100 (Countway et al., 2007). Accordingly, the soil organic matter has typically $\delta^{13}\text{C}$ values of -24‰ to -29‰ (Ongri et al., 2008), that indeed reflect the plants growing on it. On the other hand, $\delta^{15}\text{N}$ values of soil organic matter range from 2.6‰ to 6.4‰ (McCallister et al., 2004) and the C/N found in soils range from 8 to 15 (McCallister et al., 2004). Concerning algae sources, photosynthesis by freshwater phytoplankton generates POM with $\delta^{13}\text{C}$ values from -25‰ to -30‰ (Boutton, 1991; Cloern et al., 2002), $\delta^{15}\text{N}$ values from 5‰ to 8‰ (Cloern et al., 2002; McCallister et al., 2004) and C/N ratios from 4 to 10 (Meyers, 1994; Cloern et al., 2002). Therefore $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of suspended POM as well as C/N ratios will allow us to determine the source organic matter in all studied rivers.

$\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ mean values found in TSM in the Rhône River are $-27.1 \pm 0.6\text{‰}$ and $4.9 \pm 1\text{‰}$, respectively, which are within the range of those by Harmelin-Vivien et al. (2010) in 2004 ($\delta^{13}\text{C}$: $-26.6 \pm 1.2\text{‰}$ and $\delta^{15}\text{N}$: $5.7 \pm 1.8\text{‰}$) and 2005 ($\delta^{13}\text{C}$: $-27.4 \pm 1.4\text{‰}$ and $\delta^{15}\text{N}$: $4.8 \pm 1\text{‰}$). These values are also similar to those found by Bănarău et al. (2007) in Danube River, the second largest river in Europe ($\delta^{13}\text{C}$: $-27.5 \pm 0.9\text{‰}$ and $\delta^{15}\text{N}$: $4.9 \pm 1.5\text{‰}$). Interestingly, $\delta^{15}\text{N}$ of TSM in the Têt River increased

BGD

10, 13277–13316, 2013

Biogeochemical characterization of the riverine organic matter

M. Higuera et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

significantly from 2006 ($\delta^{15}\text{N}$ of $1.9 \pm 1.2\text{‰}$, Kerhervé, personal communication, 2007) to 2008 ($\delta^{15}\text{N}$ of $7.5 \pm 1.9\text{‰}$, this study). As will be discussed later, this isotopic shift is probably related to the construction in 2008 of a new Wastewater Treatment Plant (WWTP) for the district of Perpignan city.

The isotopic composition of POC and PN as well as the C/N ratio were highly variable during the investigated year and between rivers (Fig. 9a–c), which suggests that different sources of POM dominate during the survey. The $\delta^{13}\text{C}$ values were specially variable in the Hérault, Aude, Fluvia and Tordera rivers, while rather constant values were found throughout the survey in the Rhône, Orb, Têt and Ter rivers (Fig. 9a). This discrepancy between rivers is due the ^{13}C -depleted values (-29.4 to -33.2‰) recorded during summer- early autumn months (July to October 2009) in the Hérault, and Aude rivers, as well as, in Tordera River (also in November and December 2008). During those months very low water discharges and high water temperatures (up to 25°C) were recorded. These conditions may have favoured the proliferation of phytoplankton thus increasing in POC contents (up to 15.5 %, 9.3 % and 22.4 % in the Hérault Aude and Tordera rivers, respectively) and decreasing the $\delta^{13}\text{C}$ ratio ($\sim -30\text{‰}$). In warm and stagnant waters from the downstream part (the most human influenced area) of coastal rivers, nutrients is large enough to provok algae productions (Garcia-Esteves, 2005; Ludwig et al., 2003). Aquatic plants primarily derive their carbon from dissolved inorganic carbon (DIC) mainly originated from dissolved atmospheric CO_2 or plant respiration. The freshwater will become rapidly depleted in ρCO_2 . Dissolved atmospheric CO_2 has a $\delta^{13}\text{C}$ composition near 0‰ for waters with $\text{pH} > 7$ (as all the studied coastal rivers, Kerhervé, personal communication, 2007). The depleted $\delta^{13}\text{C}$ values ($< -30\text{‰}$) found during low water stages were therefore produced by an other DIC source. Addition of respired CO_2 , characterized by a similar $\delta^{13}\text{C}$ than the C source (i.e. C3 plant), usually decreases the $\delta^{13}\text{C}$ of DIC (Fry and Sherr, 1984; Kendall et al., 2001). Leaf litter and fine root detritus are drained from the watershed into depositional sites as streams and rivers (Nadeu et al., 2012). This organic material found within the river seston when rainfall events occurred may settle in the river sed-

Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



iment and be mineralized. As the York River, we may deduce that a net heterotrophy occurred in most of the Mediterranean coastal rivers, in spite of the freshwater algae production, and that heterotrophy induced addition of respired and ^{13}C -depleted CO_2 (Raymond et al., 2000).

5 The rivers with the smaller watershed (Fluvià and Tordera rivers), which are torrential in their character, exhibited a different temporal pattern in the origin of the POM, with ^{13}C -depleted values found in winter (Fluvià River) and spring (Tordera River). Thus, suspended particles during the long periods of low water discharges and low TSM concentrations are enriched in POC derived from autochthonous primary production ($\delta^{13}\text{C}$ from -33‰ to -29.4‰). In contrast, high water discharges, produced by rainstorm events or snowmelt, trigger a fast increase of TSM, thus reducing the POC contents (because of the dilution effect and lowered primary production) and showing enriched- ^{13}C values (from -28.1‰ to -25‰) compared to low water stages. During these periods, when the TSM concentration is higher than 50 mg L^{-1} , an averaged $\delta^{13}\text{C}$ value of $26.3 \pm 0.4\text{‰}$ is calculated in the Rhône River, whereas coastal rivers show an averaged $\delta^{13}\text{C}$ of $-26.9 \pm 1.2\text{‰}$. This POM is mainly originated from eroded soils and their C isotopic values vary within the same range (around -25.8‰) than surface soils from a small Mediterranean watershed in SE Spain (Nadeu et al., 2012). The soil end-member of coastal rivers exhibits a lower averaged $\delta^{13}\text{C}$ value than the one of the Rhône River. This difference may be explained by the importance of natural vegetation (more than 75% of the total areas) in watersheds of coastal rivers (Lespinas et al., 2010). In the Mediterranean region, plant remains are deposited and accumulated on the ground during long drought periods before they are carried into streams and rivers.

25 The $\delta^{15}\text{N}$ values of POM show a clear difference between studied rivers. POM in rivers draining the Alps and the Central Massif show rather constant $\delta^{15}\text{N}$ values (mean $\delta^{15}\text{N}$ of $5.4 \pm 1.4\text{‰}$) while POM in rivers draining the Pyrenees and Montseny Massif exhibit the highest and most variable $\delta^{15}\text{N}$ ratios (mean $\delta^{15}\text{N}$ of $9.2 \pm 2.6\text{‰}$), except Fluvià River that is more constant (mean $\delta^{15}\text{N}$ of $8.1 \pm 1\text{‰}$) (Fig. 9b). The maximum $\delta^{15}\text{N}$ values were obtained in Têt, Ter and Tordera rivers (10.9, 16.8 and 14.4‰, re-

BGD

10, 13277–13316, 2013

Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

spectively) coinciding with a lowest Q as well as the highest POC and PN contents. This $\delta^{15}\text{N}$ enrichment during low water discharge is probably influenced by human activities and the denitrification processes occurring in WWTPs. The dissolved inorganic nitrogen (DIN) present in sewage effluents is usually enriched with ^{15}N (Bottcher et al., 1990; Kendall et al., 2001; Cole et al., 2006). During low water stages the contribution of sewage inputs increases (Garcia-Esteves, 2005) and eutrophication processes such as denitrification may occur in the river as in the water treatment plants. This process removes ^{14}N -nitrate at a faster rate than ^{15}N -nitrate because ^{14}N is lighter and easier to metabolize (Heaton, 1986). The remaining nitrate in sewage effluent is therefore ^{15}N -enriched and organic nitrogen compounds produced by phytoplankton cells will also tend to become enriched in ^{15}N (Costanzo et al., 2005) with $\delta^{15}\text{N}$ values reaching up 10 or 20‰ in polluted rivers (Kreitler et al., 1978; Macko and Ostrom, 1994; McClelland and Valiela, 1998). Therefore, the ^{15}N -enriched POM in Têt, Ter and Tordera rivers reflects the importance of urban activities in the lowest part of their watersheds.

Overall, the origin and therefore the quality of suspended POC and PN in rivers discharging to the NW Mediterranean Sea strongly depend on the water stages (low vs. high water flows) and at the last instance on the meteorological events. The principal components analysis, a multivariate statistical analysis method (Fig. 5) confirms the relationship between quantitative (Q and TSM) and qualitative (%POC, %PN, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) parameters. An increase of TSM concentration during high water flows coincides with a decrease of %POC and %PN. During these high water stages TSM exhibit a clear increase in $\delta^{13}\text{C}$ values and a decrease in $\delta^{15}\text{N}$ values which highlights the large contribution of C3 plants remains and soils (terrestrial source). This pattern of high water flows is mainly characterized by the Rhône River (Fig. 5), the largest studied river which exhibits the most constant quality of POM throughout the year. On the other hand, the principal components analysis exhibit that low water flows are correlated with an organic rich material mainly originated from ^{13}C -depleted freshwater algae or plants. This pattern of low water range is mainly associated with the smallest watershed's rivers (Fluvià and Tordera rivers).

Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



5 Conclusions

This study has allowed to simultaneously assess for the first time the variations of the quantity and origin of the POM discharged by eight rivers into the NW Mediterranean Sea and their relation to the water flows. Our main conclusions are as follows.

1. The large Rhône River is characterized by high and relatively constant water flow and TSM concentrations in opposition to coastal rivers characterized by long period of low water stages and eutrophication processes, as well as, by ephemeral high flows, produced by rainstorm events. Coastal rivers draining the Central Massif (Hérault, Orb and Aude rivers) are more impacted by *Cévenol* events triggered by S–SE winds, whereas coastal rivers draining the Pyrenees and the Montseny Massif (Têt, Fluvià, Ter and Tordera rivers) are more affected by *Llevantada* events triggered by E–NE winds. These rainstorms produce a fast increase of Q , which remove the sediments accumulated during the low water flow periods, thus increasing the TSM concentration in coastal rivers.
2. This study shows that riverine inputs to the North Western Mediterranean are not homogeneous throughout the survey in terms of quality of organic matter discharged from land to sea.
 - The coastal rivers transport suspended particles that are enriched in organic compounds (POC \sim 8.5 % and PN \sim 1.5 %) compared to the Rhône River material (POC \sim 3.6 % and PN \sim 0.5 %). This discrepancy reflect a more pronounced eutrophication of waters in coastal rivers that may be due to the reduction of the water discharge for all studied rivers as observed throughout Mediterranean rivers over the 40 last years by Ludwig et al. (2003). This decrease of Q may be directly related to the temperature increase (mean annual: 1.5 °C during 40 yr period), as well as, the increasing use of water for human activities (Lespinas et al., 2010). The decrease of precipitation during

BGD

10, 13277–13316, 2013

Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

certain periods of the year in the upstream watersheds may also affect the water flows and favour the eutrophication of waters in coastal rivers.

- The isotopic ratios ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of POM reflect a mixture of terrestrial (plants remains and soils) and algae (freshwater phytoplankton) sources with different proportions according to the river and the water flow. The coastal rivers, characterized by long periods of low water stages, are often places where eutrophication processes enhance the production of freshwater phytoplankton, as indicated by high POC and PN contents as well as ^{13}C -depleted ($\sim -30\text{‰}$) and ^{15}N -enriched ($> 8\text{‰}$) values. During high flows (rainfalls and snowmelt), the isotopic ratios ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of coastal rivers (-26.9‰ and 4.7‰ , respectively) tend to isotopic values of the Rhône River (-26.3‰ and 3.8‰). These ratios express an organic-poor material mainly associated with soils and plant remains.

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Biogeochemical characterization of the riverine organic matter

M. Higuera et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



References

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BGD

10, 13277–13316, 2013

Biogeochemical characterization of the riverine organic matter

M. Higuera et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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M. Higuera et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

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Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Biogeochemical characterization of the riverine organic matter

M. Higuera et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

Table 1. Water discharge (Q), total suspended matter (TSM), suspended POC and PN, their stable isotopes ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) and atomic C/N ratios are the biogeochemical parameters measured in all studied rivers from November 2008 to December 2009. The Q data are extracted from different data basis: *Compagnie Nationale du Rhône* (Rhône), *Banque Hydro France* (Hérault, Orb, Aude and Têt) and *Agència Catalana de l'Aigua* (Fluvià, Ter and Tordera).

	Rhône	Hérault	Orb	Aude	Têt	Fluvià	Ter	Tordera
Q (m^3s^{-1})								
Mean	1386.3	34.1	18.3	28.2	5.0	3.5	10.8	3.0
Standard Deviation	740.7	71.2	27.4	37.0	7.2	9.8	12.5	5.3
Maximum	4847.7	687.0	280.0	261.0	56.9	155.9	118.7	50.3
Minimum	308.5	1.4	3.9	0.0	0.0	0.2	2.3	0.0
TSM conc. (mgL^{-1})								
Mean	71.9	6.1	9.2	26.1	28.7	10.3	16.1	14.6
Standard Deviation	146.5	14.4	15.7	49.0	56.5	22.2	7.7	27.1
Maximum	488.7	57.1	60.8	194.5	223.1	86.5	28.4	103.4
Minimum	5.5	2.2	2.4	5.4	4.2	0.5	3.1	0.8
POC contents (%)								
Mean	3.6	8.4	7.8	4.7	8.0	11.4	7.7	11.9
Standard Deviation	1.6	4.3	2.2	2.1	3.4	4.1	1.3	6.0
Maximum	6.7	15.5	11.5	9.3	15.8	22.0	10.0	23.5
Minimum	1.2	2.7	3.8	1.1	3.7	5.7	5.8	3.8
PN contents (%)								
Mean	0.5	1.7	1.8	1.0	1.6	1.6	1.0	1.7
Standard Deviation	0.3	1.2	0.8	0.6	0.7	0.7	0.2	1.2
Maximum	1.1	3.9	3.3	2.6	3.3	3.5	1.6	4.6
Minimum	0.1	0.3	0.6	0.2	0.8	0.9	0.7	0.4
$\delta^{13}\text{C}$ (‰)								
Mean	-27.1	-28.6	-27.0	-28.4	-26.2	-28.7	-27.4	-28.6
Standard Deviation	0.6	1.5	0.3	1.8	0.8	1.4	0.6	1.6
Maximum	-26.1	-26.9	-26.5	-26.3	-24.5	-26.4	-26.2	-26.4
Minimum	-27.9	-31.6	-27.6	-33.2	-27.3	-31.0	-28.4	-33.0
$\delta^{15}\text{N}$ (‰)								
Mean	5.0	5.8	4.6	6.2	7.6	8.1	10.2	9.7
Standard Deviation	1.0	1.4	1.1	2.2	2.0	1.0	2.9	2.9
Maximum	6.4	8.9	6.3	11.9	10.9	9.8	16.8	14.4
Minimum	3.1	4.6	1.9	4.3	4.8	6.1	6.5	4.8
C/N ratio								
Mean	8.2	6.6	5.8	6.3	5.9	7.7	9.4	9.2
Standard Deviation	2.5	2.1	1.9	1.4	1.3	1.2	1.5	2.2
Maximum	14.7	11.1	9.8	8.9	9.3	10.4	13.3	12.0
Minimum	10.5	4.1	3.0	4.2	4.0	5.6	6.3	2.8

Biogeochemical characterization of the riverine organic matter

M. Higuera et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 2. TSM and POC annual estimated fluxes (2008–2009) of each studied river calculated from 14 samples using power equations: $TSM = a \cdot Q^b$ and $POC\% = a \cdot TSM^b$, where a and b are regression coefficients. Fluxes are only calculated in rivers with a p value statistically significant (p value < 0.05).

TSM vs Q							
River	Equation	n	Parameters		R^2	p value	TSM Flux (10^6Tyr^{-1})
Rhône	$TSM = 7.9 \cdot 10^{-7} Q^{2.4}$	14	7.9×10^{-7}	2.4	0.8	7×10^{-6}	2.8
Hérault	$TSM = 0.8 Q^{0.5}$	14	0.8	0.5	0.6	0.0010	0.012
Orb	$TSM = 5.0 Q^{-0.1}$	14	5.0	-0.1	–	–	–
Aude	$TSM = 7.1 Q^{0.2}$	14	7.1	0.2	0.1	0.3	–
Têt	$TSM = 6.1 Q^{0.8}$	14	6.1	0.8	0.5	0.0040	0.008
Fluvià	$TSM = 0.5 Q^{1.8}$	14	0.5	1.8	0.7	0.0001	0.090
Ter	$TSM = 3.1 Q^{0.6}$	14	3.1	0.6	0.3	0.04	0.008
Tordera	$TSM = 5.4 Q^{0.5}$	14	5.4	0.5	0.5	0.0040	0.001

POC vs TSM							
River	Equation	n	Parameters		R^2	p value	POC Flux (10^4Tyr^{-1})
Rhône	$\%POC = 7.6 TSM^{-0.3}$	14	7.6	-0.3	0.6	0.0010	5.8
Hérault	$\%POC = 12.2 TSM^{-0.4}$	14	12.2	-0.4	0.3	0.04	0.06
Orb	$\%POC = 7.8 TSM^{-0.03}$	14	7.8	-0.03	–	–	–
Aude	$\%POC = 17.1 TSM^{-0.5}$	14	17.1	-0.5	0.9	$7 \cdot 10^{-6}$	0.06
Têt	$\%POC = 17.1 TSM^{-0.3}$	14	17.1	-0.3	0.5	0.0040	0.04
Fluvià	$\%POC = 13.7 TSM^{-0.2}$	14	13.7	-0.2	0.5	0.0040	0.3
Ter	$\%POC = 7.7 TSM^{-0.01}$	14	7.7	-0.01	–	–	–
Tordera	$\%POC = 15.8 TSM^{-0.3}$	14	15.8	-0.3	0.5	0.0040	0.01

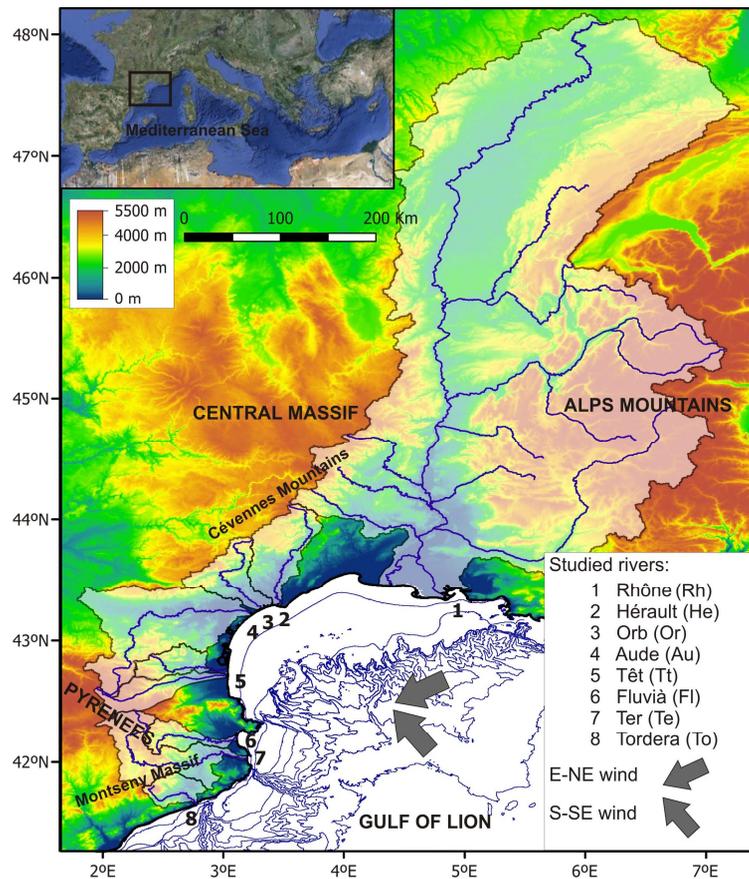


Fig. 1. Location of the study area with the eight studied rivers and their watersheds, the orography and the main wind directions.

**Biogeochemical
 characterization of
 the riverine organic
 matter**

M. Higuera et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

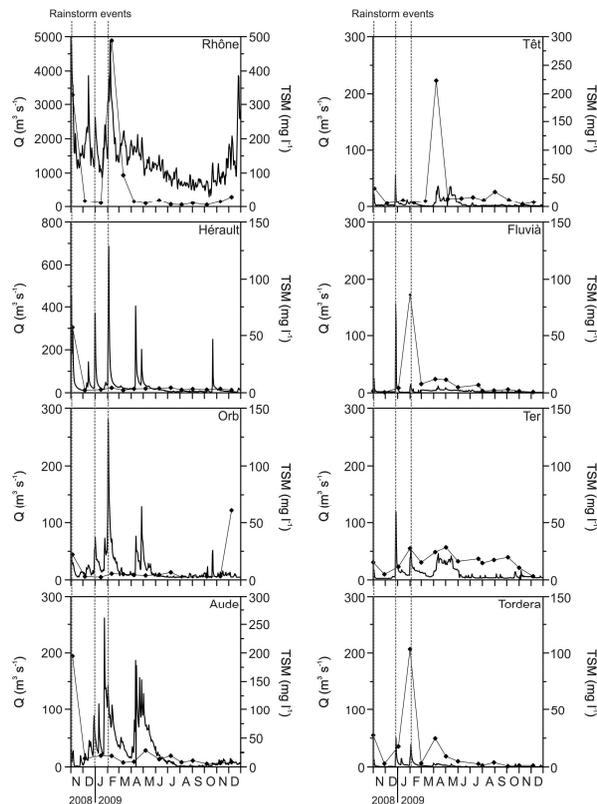


Fig. 2. Average daily water discharge (Q) measured at the gauging station of each studied river from November 2008 to December 2009 by *Compagnie Nationale du Rhône* (Rhône River), *Banque Hydro France* (Hérault, Orb, Aude and Têt rivers) and *Agència Catalana de l'Aigua* (Fluvià, Ter and Tordera rivers). The three storm events (November 2008, December 2008 and February 2009) that impacted the study area are shown as a dotted line. Plots show the temporal variability of total suspended matter (TSM) concentrations with corresponding average daily water discharge.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

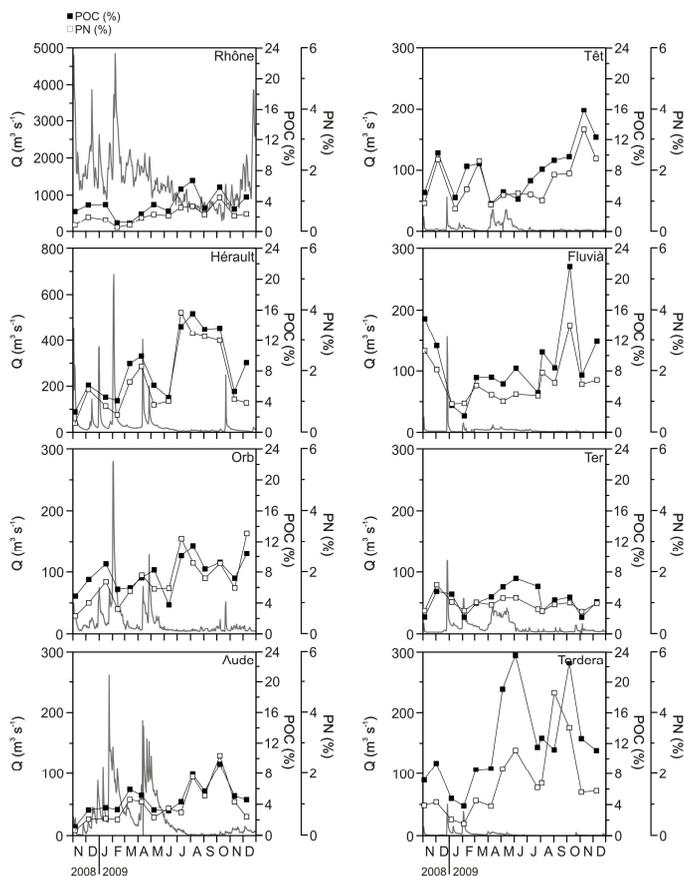


Fig. 3. Temporal variability of particulate organic carbon (POC) and nitrogen (PN) contents (in percentage) with the corresponding average daily water discharges (Q) of the eight studied rivers from November 2008 to December 2009.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Biogeochemical characterization of the riverine organic matter

M. Higuera et al.

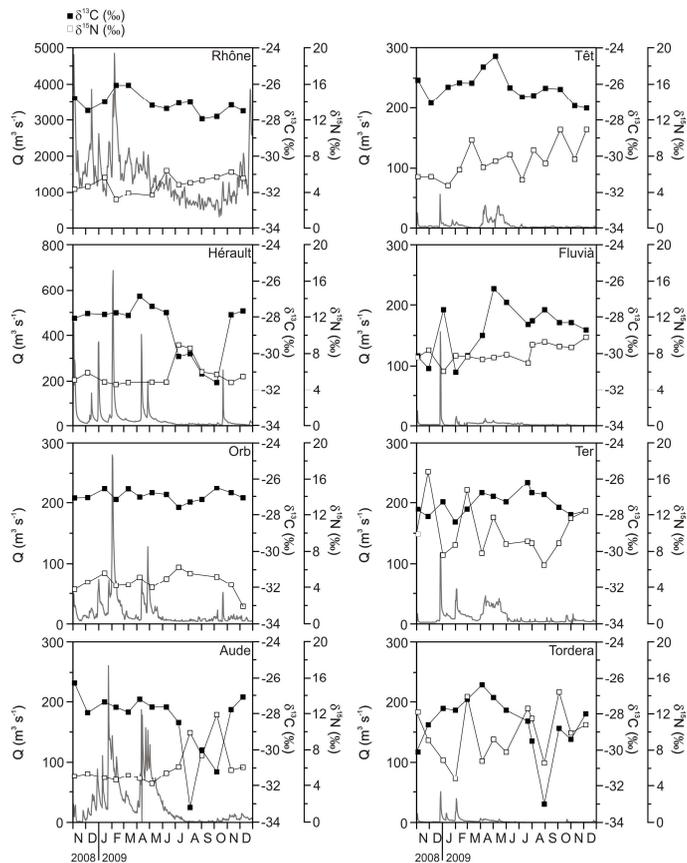


Fig. 4. Temporal variability of the stable isotopes ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) with the corresponding average daily water discharges (Q) of the eight studied rivers from November 2008 to December 2009.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

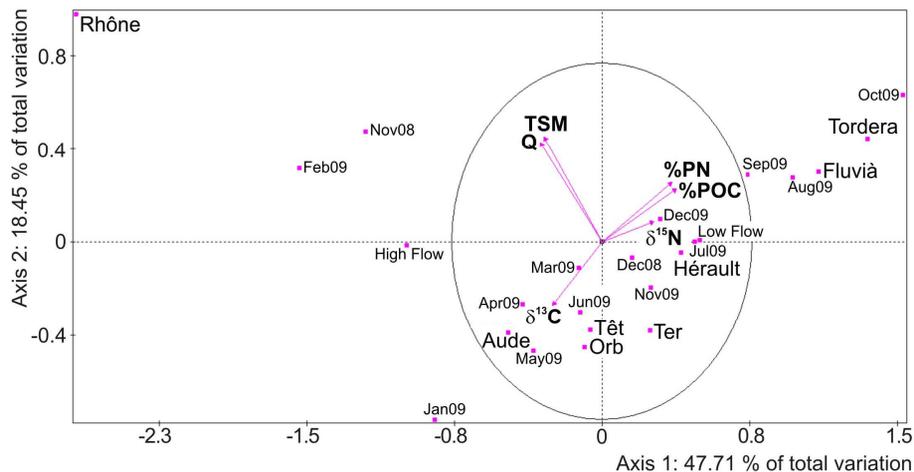


Fig. 5. Projection of the six active numerical (Q : water discharge, TSM: Total suspended matter, %POC and %PN: percentage of particulate organic carbon and nitrogen and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$: stable isotopes) and 3 illustrative categorical variables (month, river and water discharge coded in two modalities: low and high) on the first factorial plane of the principal components analysis (PCA).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Biogeochemical characterization of the riverine organic matter

M. Higuera et al.

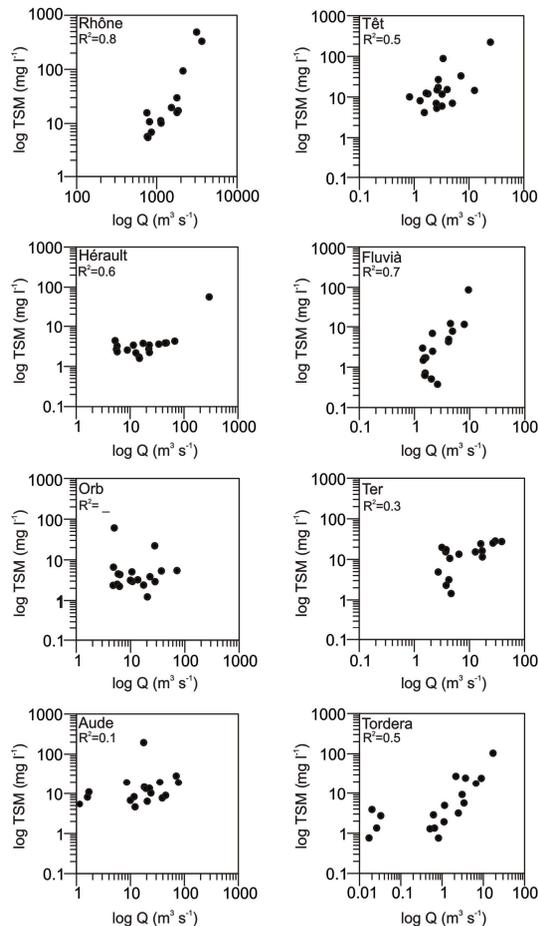


Fig. 6. Logarithmic plot between total suspended matter (TSM) concentration and average daily water discharge (Q) with R^2 values obtained using the sediment rating curve: $TSM = a \cdot Q^b$, where a and b are regression coefficients.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

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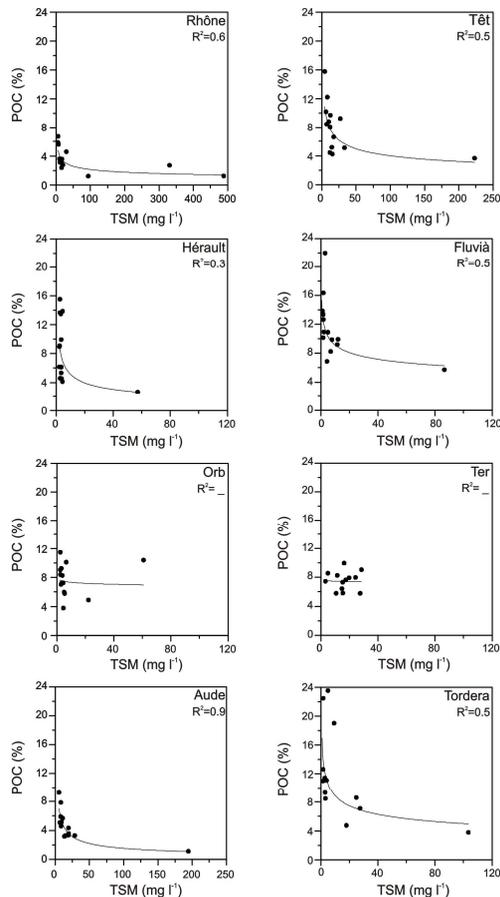


Fig. 7. Relationships between total suspended matter (TSM) concentration and particulate organic carbon (POC) contents (in percentage) with R^2 values obtained using the power equation: $POC\% = a \cdot TSM^b$, where a and b are regression coefficients.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Biogeochemical characterization of the riverine organic matter

M. Higueras et al.

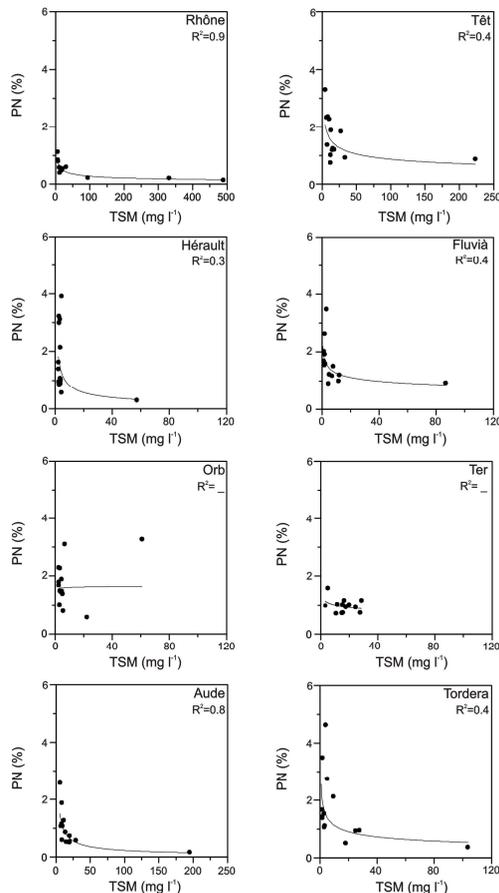


Fig. 8. Relationships between total suspended matter (TSM) and particulate nitrogen (PN) contents (in percentage) with R^2 values obtained using this equation: $PN\% = a \cdot TSM^b$, where a and b are regression coefficients.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

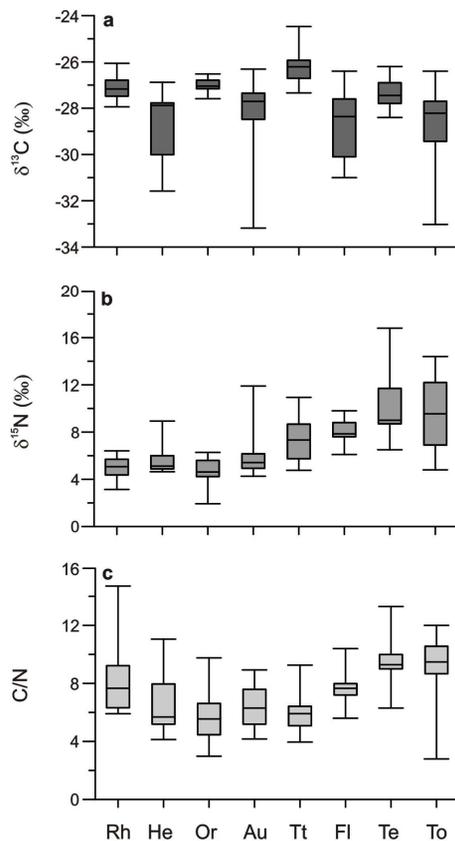


Fig. 9. Spatial variations of the stable isotopes $\delta^{13}\text{C}$ (a) and $\delta^{15}\text{N}$ (b) and C/N ratio (c) from November 2008 to December 2009. The boxplot shows the extreme values, the quartiles and the mean value of each river. Rh: Rhône, He: Hérault, Or: Orb, Au: Aude, Tt: Têt, Fl: Fluvià, Te: Ter and To: Tordera.