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Toward a typology of river functioning: a comprehensive study of POM composition at multi-rivers scale

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Abstract

In riverine systems, particulate organic matter (POM) originates from various sources, each having its proper dynamics related to production, decomposition, transport and burial. There is a significant amount of spatiotemporal heterogeneity in the POM pool. The current study, based on C and N elemental and isotopic ratios, applies Bayesian mixing models associated with statistical multivariate analyses to 1) quantify and examine relationships between POM composition and environmental forcings, and 2) draw a typology of river functioning based on POM composition and its seasonal dynamics. Twenty-three rivers of temperate climate accounting for a large diversity of environmental conditions were sampled fortnightly to monthly for one to seven years at the River-Estuary Interface (REI). Phytoplankton and labile terrestrial material were present in all rivers, contrary to sewage and refractory terrestrial material that were present in only a few. At the twenty-three studied rivers scale, POM sources are strongly related to watershed characteristics, phytoplankton being associated with agricultural surfaces and labile terrestrial material to soil organic carbon content and erosion rate. Overall, seasonal variations of phytoplankton, labile and refractory terrestrial material were mainly related to drivers of phytoplankton growth, river flow, and sediment resuspension, respectively. A statistical regionalization defined four river types: (1) systems whose POM is dominated by labile terrestrial material all year long; (2) systems whose POM is composed of labile and refractory terrestrial material, in addition to phytoplankton, with variable seasonality according to rivers; systems whose POM is composed of phytoplankton and labile terrestrial material (3) without and (4) with pronounced seasonality.

This work offers a comprehensive understanding of POM composition, dynamics and drivers at the REI in temperate climates, complementing similar work dedicated to coastal systems. Future work dedicated to estuaries is called to get a comprehensive understanding of POM composition, dynamics and drivers along the Land-Ocean Aquatic Continuum.

This study examines particulate organic matter (POM) composition and dynamics in 23 temperate rivers. Carbon and nitrogen isotope analysis revealed four river types based on dominant POM sources (phytoplankton, terrestrial material). Watershed characteristics influence POM composition while seasonal variations in river flow and sediment resuspension drive POM dynamics. This study improves the understanding of river systems and calls for further studies exploring downstream estuarine functioning.

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1. Introduction

The River-Estuary Interface (REI) is a crucial biogeochemical interface for understanding the transition between continental and coastal systems, beginning at estuaries, because of its key location within the Land-Ocean Aquatic Continuum (LOAC) (Bate et al., 2002). Indeed, rivers then estuaries are important filters for matters received from land, transporting and transforming organic matter and nutrients along their courses (Bouwman et al., 2013; Dürr et al., 2011; Middelburg and Herman, 2007). These processes are fundamental in understanding global biogeochemical cycles (Regnier et al., 2013), as these matters directly fuel coastal ocean trophic networks (Dagg et al., 2004). However, in a Human-impacted world, anthropogenic activities and disturbances can modify natural matter fluxes. For example, damming rivers directly impacts nutrient flows (Wang et al., 2022) and sediment transportation (Kang et al., 2021). Indirectly, land use in river basins can lead to changes in the river matter quality (Lambert et al., 2017).

In aquatic systems, particulate organic matter (POM), i.e., non-mineral particles, is composed of different sources that originate from different compartments: phytoplankton, macrophytes from the aquatic systems as well as soil particles and plant litter from terrestrial compartments and even treated and untreated anthropogenic organic matter (Ke et al., 2019; Sun et al., 2021; Zhang et al., 2021). Depending on its composition, POM exhibits different levels of lability, i.e., different levels of biogeochemical reactivity and bioavailability. For instance, phytoplankton is usually considered mainly labile and thus highly biogeochemically reactive and bioavailable for primary consumers, while terrestrial POM is usually considered mainly refractory and thus lightly biogeochemically reactive and poorly bioavailable for the food webs (Brett et al., 2017; David et al., 2005; Etcheber et al., 2007). In other words, the determination and quantification of POM composition (i.e., the relative proportion of each source composing the POM) allow a better understanding of biogeochemical cycles and trophic ecology in aquatic systems (e.g., Grunicke et al., 2023; Minaudo et al., 2016). Nevertheless, POM composition and concentration are not only involved in biogeochemical and biological processes (e.g., primary production, remineralization, feeding) but undergo other processes inside and at the interface of the aquatic compartment (Canuel and Hardison, 2016). River hydrodynamics is one of the main drivers of POM composition and concentration, leading to great variabilities in terrestrial material quality and quantity (Dalzell et al., 2007; Lebreton et al., 2016; Marshall et al., 2021), possibly leading to changes in source origins (Arellano et al., 2019; Barros et al., 2010). Also, changes in anthropic pressures can change POM composition and concentration and their seasonal variations, like a decrease in nutrient load (Minaudo et al., 2015).

This dependency of POM composition and concentration on physical, biogeochemical and biological processes and their responses to environmental conditions and characteristics (Bonin et al., 2019; Falkowski et al., 1998; Field et al., 1998; Galeron et al., 2017; Goñi et al., 2009;

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Lebreton et al., 2016) may lead to distinguishing different typology of rivers, i.e., the likeliness of rivers to carry preferential sources. For instance, highly turbid systems are more likely to carry refractory materials (Savoye et al., 2012), while eutrophicated rivers carry high biomass of phytoplankton (Hounshell et al., 2022; Minaudo et al., 2015) and contrasted processes can lead to a mixture between different detrital sources, as soil matter vs. fresh terrestrial plants (Ogrinc et al., 2008). However, to date, no study clearly determined typologies of rivers based on POM composition and its seasonal variability.

To distinguish POM sources and quantify their contribution to POM composition, different tools such as elemental and isotopic ratios, pigments or specific compounds like fatty acids or alkanes can be used (e.g., Chevalier et al., 2015; Liénart et al., 2020, 2017; Savoye et al., 2012). Elemental and isotopic ratios are usually considered robust and allow the quantification of POM composition in this kind of study (e.g., Liénart et al., 2016; Onstad et al., 2000; Wang et al., 2021). Indeed, they usually allow the discrimination of, e.g., riverine phytoplankton, terrestrial POM and wastewater POM (Ke et al., 2019) and they can be used for running mixing models that quantify the proportion of the different sources into a POM mixture (Parnell et al., 2013). However, studies using mixing models for quantifying POM composition in river systems are still scarce (e.g., Ferchiche et al., 2025, 2024; Kelso and Baker, 2022, 2020; Zhang et al., 2021).

Within the scope of better understanding the role of the LOAC in modifying matter fluxes and quality, the present study gathered published data and results from 23 rivers at the river-estuary interface with the aim of 1) quantifying the POM composition each river, 2) describing the seasonal variations of this composition, 3) determining the drivers of the seasonal variability within each river and the spatial variability among the 23 rivers, and then 4) determining a typology of rivers according to their POM composition and dynamics. This study is the first to precisely quantify POM composition in numerous and various temperate river systems and classify river types according to POM composition and dynamics.

2. Material and methods

Twenty-three temperate rivers were studied at their river-estuary interface (i.e., right upstream of the tidal influence). All the data come from published studies or national open databases. To minimize the heterogeneity of the datasets in terms of sampling strategy, we have considered for this study the datasets only when 1) C/N ratio along with isotopic ratio of carbon and/or nitrogen were available, 2) particulate matter characteristics like, suspended particulate matter (SPM), particulate organic carbon (POC), particulate nitrogen (PN), chlorophyll *a* (chl *a*) were also available, 3) datasets exhibited at least a monthly temporal resolution for one full year. When needed, published datasets were completed and harmonized thanks to national databases.

2.1. Study sites

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The studied rivers and associated watersheds are all located in France (except the upper basin of the Rhône River) and distributed in all regions of the mainland. Three, fifteen and five of these rivers flow into the English Channel, the Atlantic Ocean and the Mediterranean Sea (Fig. 1). They encompass large gradients of environmental characteristics (Tab. 1). For instance, the Loire River is one of the largest in Europe (length: 1006 km; watershed: 117,356 km²), while the littlest studied river is a very small stream of the Arcachon lagoon (length: 3 km; watershed: 18 km²). They encompass large gradients of river flow (annual mean: 0.3 m^3/s – 1572 m^3/s), turbidity (SPM annual mean: 2.7 mg/l – 40.9 mg/l) and trophic status (from oligotrophic to eutrophic rivers; chl *a* annual mean: 0.4 µg/l – 57.1 µg/l). At last, they undergo a gradient of anthropic pressures as illustrated by the proportion of artificial surfaces (0.1 % – 5.6 %) and agricultural areas (0 % – 86 %) in the watersheds (Fig. 1).

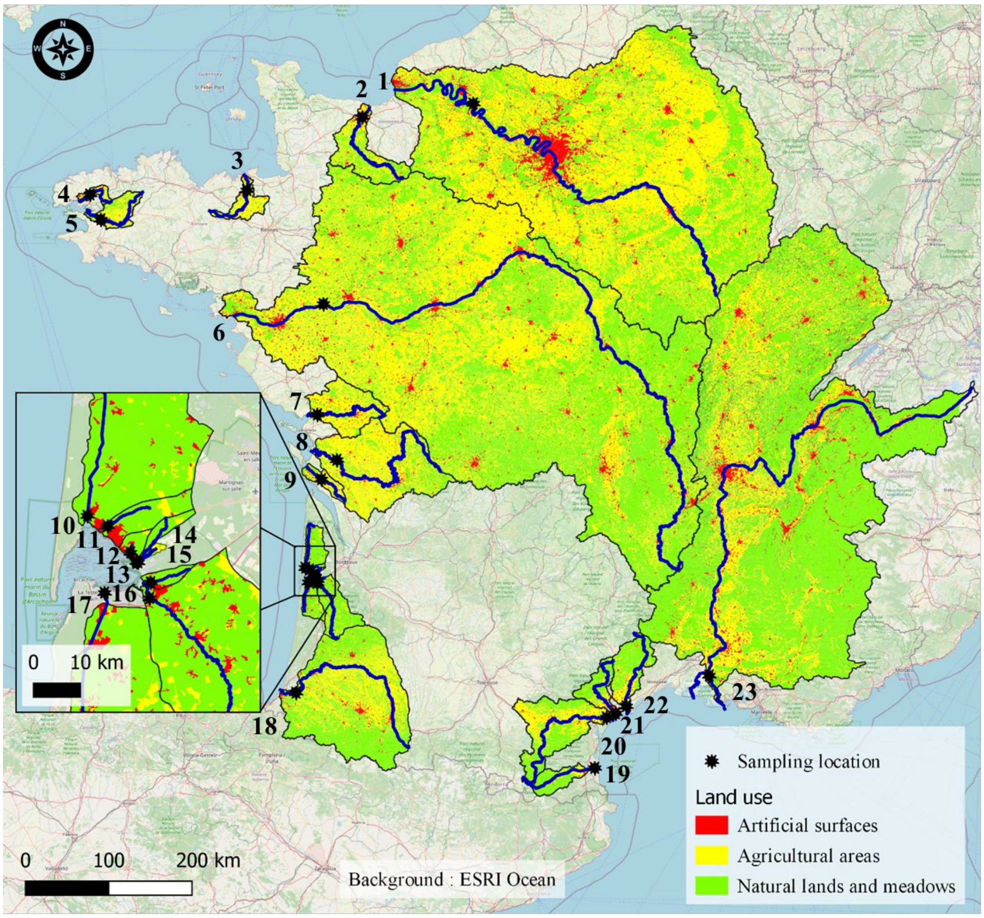

Figure 1 Studied rivers (thick blue lines), sampling locations (black stars) and watersheds (thin black lines) including the main land uses (red, yellow and green colors). 1: Seine; 2: Orne; 3:

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Rance; 4: Elorn; 5: Aulne; 6: Loire; 7: Sèvre niortaise; 8: Charente; 9: Seudre; 10: Canal du Porge; 11: Cirès; 12: Milieu; 13: Lanton; 14: Renet; 15: Tagon; 16: Leyre; 17: Canal des Landes; 18: Adour; 19: Têt; 20: Aude; 21: Orb; 22: Hérault; 23: Rhône.

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Table 1 Overview of river samplings and characteristics. Values are given as annual mean over the study period for river flow, temperature, suspended particulate matter (SPM) and chlorophyll *a* (chl *a*). Id: identification number; Number: number of sampling dates. River types were defined within the scope of the present study (see section 3.4).

River	Id	River type	Sampled period	Sampling Periodicity	Number	Latitude	Longitude	River length (km)	Catchment area (km²)	River flow (m3/s)	Water temperature (°c)	SPM (mg/l)	Chl *a* (µg/l)	References
Seine	1	IV	06/2014 to 06/2015	monthly	13	49.3067	1.2425	774	79000	496	15.0	21	2.8	Liénart et al., 2017, 2018
Orne	2	III	06/2014 to 06/2015	monthly	13	49.1797	-0.3491	169	2932	16	14.5	11	1.8	Liénart et al., 2017, 2018
Rance	3	IV	06/2014 to 05/2015	monthly	12	48.4916	-2.0014	103	1195	1.37	15.1	21	57.1	Liénart et al., 2017, 2018
Elorn	4	IV	01/2014 to 06/2015	monthly	17	48.4505	-4.2483	56	385	6	12.3	16	3.0	Liénart et al., 2017, 2018
Aulne	5	IV	01/2014 to 06/2015	monthly	17	48.2127	-4.0944	144	1875	30	14.4	7	3.3	Liénart et al., 2017, 2018
Loire	6	IV	10/2009 to 07/2012	bi-monthly	67	47.3920	-0.8604	1006	117356	630	14.1	19	18.7	Ferchiche et al., 2024
Sèvre	7	IV	03/2014 to 03/2015	monthly	13	46.3153	-1.0039	158	3650	3.72	15.7	13	3.8	Liénart et al., 2017, 2018
Charente	8	III	03/2014 to 03/2015	monthly	13	45.8680	-0.7131	381	9855	68	15.1	13	1.3	Liénart et al., 2017, 2018
Seudre	9	I	03/2014 to 09/2015	monthly	15	45.6740	-0.9331	68	855	1.81	14.3	17	0.5	Liénart et al., 2017, 2018
Porge	10	III	01/2008 to 02/2009	monthly	14	44.7898	-1.1612	57	222	3.48	13.3	12	5.0	Polsenaere et al., 2013
Cirès	11	I	02/2008 to 02/2009	monthly	13	44.7598	-1.1107	12	45	0.58	12.2	5	0.4	Polsenaere et al., 2013
Renet	12	I	02/2008 to 02/2009	bi-monthly	23	44.7144	-1.0441	3	18	0.56	12.9	10	0.6	Polsenaere et al., 2013
Lanton	13	I	02/2008 to 02/2009	monthly	13	44.7002	-1.0244	15	36	0.26	12.5	11	1.2	Polsenaere et al., 2013
Milieu	14	I	02/2008 to 02/2009	monthly	13	44.6973	-1.0225	7	21	0.58	12.7	7	0.4	Polsenaere et al., 2013
Tagon	15	I	02/2008 to 02/2009	bi-monthly	26	44.6590	-0.9891	10	30	0.64	12.6	13	1.3	Polsenaere et al., 2013
Leyre	16	I	01/2008 to 03/2010 and 02/2014 to 02/2015	bi-monthly or monthly	59	44.6263	-0.9961	116	1700	17	13.0	11	0.9	Dubois et al., 2012 / Polsenaere et al., 2013 / Liénart et al., 2017, 2018
Landes	17	III	02/2008 to 02/2009	monthly	12	44.6169	-1.1091	14	117	0.49	14.1	3	1.1	Polsenaere et al., 2013
Adour	18	III	04/2013 to 06/2014 and 05/2017 to	monthly	24	43.4988	-1.2949	308	16912	516	14.0	48	2.4	Liénart et al., 2016 / Deborde, 2019
Têt	19	II	01/2006 to 05/2010	monthly	52	42.7137	2.9935	115	1369	23	15.7	8	NA	Higueras et al., 2014
Hérault	20	II	01/2006 to 05/2010	monthly	52	43.3594	3.4354	148	2582	53	16.0	7	NA	Higueras et al., 2014
Orb	21	II	01/2006 to 05/2010	monthly	52	43.2850	3.2813	136	1585	23	15.7	8	NA	Higueras et al., 2014
Aude	22	II	01/2006 to 05/2010	monthly	52	43.2442	3.1527	223	5327	40	14.2	31	NA	Higueras et al., 2014
Rhône	23	II	12/2003 to 01/2011	monthly	105	43.6787	4.6212	812	95590	1572	15.9	41	1.9	Harmelin-Vivien et al., 2010 / Cathalot et al., 2013 / Higueras et al., 2014

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2.2. Data origin

Regarding the core parameters (C/N ratio, $\delta^{13}C$, $\delta^{15}N$, water temperature, SPM, POC, PN, chl *a*), most of the data sets come from published studies (Canton et al., 2012; Cathalot et al., 2013; Dubois et al., 2012; Ferchiche et al., 2024; Harmelin-Vivien et al., 2010; Higueras et al., 2014; Liénart et al., 2016, 2017, 2018; Polsenaere et al., 2013), while most of additional parameters come from national databases (Tab. A1). When not available in the cited studies, concentrations of SPM, NO_3^-, NH_4^+ and PO_4^{3-}, pH and water temperature were retrieved from the *Naïades* database (https://naiades.eaufrance.fr/, consulted the 07/10/2023). Note that these parameters were not necessarily measured or sampled exactly at the same location or date for *Naïades* than in the cited studies. In that case, the location was chosen as close as possible to the study location and data values were time-interpolated to match the study date. Meteorological variables (air temperature, zonal and meridional wind, irradiance) come from Météo France, the French meteorological service. Wind data was received originally as direction and speed. To remove the angular bias, they were combined using scalar products to get zonal and meridional wind speeds, which range between minus and plus infinity (see Lheureux et al., 2022, for more details). River flows were retrieved from the *Banque Hydro* database (https://www.hydro.eaufrance.fr/, consulted the 07/10/2023) or from Polsenaere et al. (2013) for the small streams. Land use proportions originate from the national Corine Land Cover database (https://www.statistiques.developpement-durable.gouv.fr/corine-land-cover-0, consulted the 10/01/2024). Soil organic carbon data originate from the SoilTrEC database (https://esdac.jrc.ec.europa.eu/content/predicted-distribution-soc-content-europe-based-lucas-biosoil-and-czo-context-eu-funded-1, consulted the 10/01/2024). Net erosion soil data originates from the WaTEM/SEDEM database (https://esdac.jrc.ec.europa.eu/content/estimate-net-erosion-and-sediment-transport-using-watemsedem-european-union, consulted the 10/01/2024).

It should be noted that a complete study was already dedicated to the Loire River and reported as a companion article (Ferchiche et al., 2024). Consequently, the results are not reported in the present study but are used for multi-system comparisons (Fig. 5 and 7, and corresponding text).

2.3. Determination of sources signatures

To run mixing models for quantifying POM composition, it is previously needed to 1) determine sources of POM, and 2) associate elemental and isotopic signatures to these sources. In riverine systems, phytoplankton and terrestrial POM are the main sources that are usually considered as fueling the POM (e.g., Ferchiche et al., 2024; Pradhan et al., 2016; Sarma et al., 2014). Nevertheless, sewage POM may also contribute (Higueras et al., 2014). Consequently, phytoplankton, terrestrial POM and sewage POM were considered as potential sources in this study.

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Phytoplankton cannot be easily picked up from bulk particles to measure its elemental and isotopic ratios. Therefore, the method developed and used by Savoye et al. (2012), Liénart et al. (2017) and Ferchiche et al. (2024) was applied here. It consists of determining the elemental and isotopic ratios from a subset of the bulk dataset. Briefly, phytoplankton-dominated POM is characterized by a low POC/chl *a* ratio (≤ 200 or even ≤ 100 g/g; Savoye et al., 2003 and references therein). Thus, elemental and isotopic ratios of samples exhibiting a low POC/chl *a* ratio can be considered as good estimates of phytoplankton elemental and isotopic ratios. When the POC/chl *a* ratio is not available, samples exhibiting a high PN/SPM ratio can be used. Additional constraints may be used to minimize potential overlap between phytoplankton and terrestrial elemental and isotopic signatures. Phytoplankton elemental and especially isotopic ratios may deeply vary over time and space depending on primary production intensity and potential limiting factors, nutrient origin, etc. (e.g., Miller et al., 2013; Savoye et al., 2003). When existing, this variability has to be taken into account to avoid using elemental and isotopic signatures that are not valid at the time or location of the sampling. This could be performed by using regressions between elemental and/or isotopic ratios and environmental variables (see Ferchiche et al., 2024; Liénart et al., 2017; Savoye et al., 2012). At last, when no samples exhibit a low POC/chl *a* ratio, samples exhibiting the lowest (even if high) POC/chl *a* ratios can be used but the data should be firstly corrected from the contribution of the terrestrial POM using Equations 1-3.

$$\delta^{13}C_{sample} = ([POC]_{phytoplankton} \times \delta^{13}C_{phytoplankton} + [POC]_{terrestrial} \times \delta^{13}C_{terrestrial}) / [POC]_{sample} \quad \text{(eq. 1)}$$

$$[POC]_{phytoplankton} = [chl\ a]_{sample} \times (POC/chl\ a)_{mean} \quad \text{(eq. 2)}$$

$$[POC]_{terrestrial} = [POC]_{sample} - [POC]_{phytoplankton} \quad \text{(eq. 3)}$$

where $(POC/chl\ a)_{mean}$ is the mean POC/chl *a* ratio of the samples used to determine phytoplankton signatures. Similar equations are used for the N/C ratio, $\delta^{15}N$ and C/N ratio but using PN instead of POC for $\delta^{15}N$ and C/N ratio.

Elemental and isotopic signatures of terrestrial POM can be estimated by directly measuring elemental and isotopic ratios in terrestrial materials like soil and vascular plants (e.g., Sarma et al., 2014). However, this does not take into account the reworking of this material within the river system which can affect these signatures (Hou et al., 2021). Thus, similarly to phytoplankton, elemental and isotopic signatures of terrestrial POM can be estimated using subsets of bulk data, following the approach of Savoye et al. (2012), Liénart et al. (2017) and Ferchiche et al. (2025, 2024). Terrestrial POM is usually characterized by high POC/chl *a* and C/N ratios and low POC/SPM ratios (Etcheber et al., 2007; Savoye et al., 2003 and references therein). However, during its decay in aquatic systems, terrestrial POM is colonized by bacteria (low C/N ratio) resulting in a consortium terrestrial POM + bacteria of lower C/N ratio than the original terrestrial POM (Etcheber et al., 2007; Savoye et al., 2012). Finally, one can

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discriminate two kinds of terrestrial POM: refractory terrestrial POM characterized by high POC/chl *a* and C/N ratios and very low POC/SPM ratio, and quite labile terrestrial POM characterized by high POC/chl *a* ratio, intermediate C/N ratios and low POC/SPM ratio (Etcheber et al., 2007; Savoye et al., 2012). Thus, subsets of high POC/chl *a* ratio can be selected to determine the elemental and isotopic signatures of terrestrial POM. The C/N ratio can be used to discriminate labile from refractory terrestrial POM. When no samples exhibit a high POC/chl *a* ratio, samples exhibiting the highest (even if quite low) POC/chl *a* ratio can be used but the data should be firstly corrected from the contribution of the phytoplankton POM using Equations 1-3.

Elemental and isotopic ratios of riverine POM can exhibit a departure from a simple phytoplankton-terrestrial POM mixing. In the present study, this was the case in only two rivers. For the Têt River, elemental and isotopic signature of anthropogenic POM was available in Higueras et al. (2014). It consisted of analyses of POM sampled in the wastewater treatment plant (WWTP) the closest to the sampling site. For the Orb River, the signatures were estimated using the sample exhibiting the lowest $\delta^{15}N$, typical of anthropogenic POM (Ke et al., 2019).

The estimation of POM-source signatures was performed independently for each river, except for some of the tributaries of the Arcachon Lagoon (rivers 11 to 15), where data sets were gathered, thanks to very similar characteristics (same δ13C of dissolved inorganic carbon; Polsenaere et al., 2013), to get a larger subset of data for estimating elemental and isotopic signatures more accurately. All criteria used for defining the above-described subsets are reported in Table 2.

Table 2 Elemental and isotopic signatures of POM sources and criteria used to choose the data subset to determine them. When the signature did not vary over time, average ± standard deviation are reported. When the signature did vary over time, minimum and maximum values, standard deviations as well as equations are reported. The types of mixing models performed for each river are also indicated (carbon mixing models were performed using $\delta^{13}C$ and N/C ratio or only $\delta^{13}C$; nitrogen mixing models were performed using $\delta^{15}N$ and C/N ratio; mixed mixing models were performed using $\delta^{13}C$, $\delta^{15}N$ and N/C ratio). POC% (or PN%) = Particulate Organic Carbon (or Particulate Nitrogen) to Suspended Particulate Matter ratio (%); C/N = POC/PN ratio (mol/mol); chla = chlorophyll *a* (µg/l); phaeo = phaeopigments (µg/l); conduc = conductivity (µS); temp = water temperature (°C); Q7 = mean of past seven days river flow; NO_3^- = nitrate (mg(NO_3^-)/l).

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River	Source discriminants				Model performed			Labile terrestrial matter				Refractory terrestrial matter			
	Labile terrestrial matter	Refractory terrestrial matter	Phytoplankton	WWTP's POM	Carbon	Nitrogen	Mixed	$\delta^{13}C$	$\delta^{15}N$	C/N	N/C	$\delta^{13}C$	$\delta^{15}N$	C/N	N/C
Seine	C/N > 10		POC/chla < 200		X	X		-28.5 ± 0.3	6.6 ± 0.9	10.6 ± 0.3	0.093 ± 0.002				
Orne	C/N > 11		POC/chla < 500		X	X		-28.4 ± 0.3	5.8 ± 1.0	12.4 ± 0.4	0.082 ± 0.003				
Rance	POC/chla > 200 and chla < 10		POC/chla < 150		X	X		-26.8 ± 0.2	6.1 ± 0.7	8.8 ± 0.4	0.113 ± 0.007				
Elorn	C/N > 12		POC/chla < 200		X	X		-28.4 ± 0.7	5.8 ± 0.9	13.0 ± 0.8	0.077 ± 0.005				
Aulne	C/N > 11		POC/chla < 200 and C/N < 9		X	X		-28.9 ± 0.8	5.8 ± 0.8	12.1 ± 1.1	0.08 ± 0.008				
Loire	POC/chla > 500		POC/chla < 200		X	X		-28.1 ± 0.1	5.9 ± 0.3	10.3 ± 0.2	0.097 ± 0.002				
Sèvre Niortaise	C/N > 14		POC/chla < 300		X			-28.0 ± 0.4			0.057 ± 0.040				
Charente	C/N > 12		POC/chla < 300		X	X		-29.0 ± 0.4	4.7 ± 0.2	14.5 ± 0.5	0.069 ± 0.002				
Seudre	POC/chla > 2000 and C/N > 12		POC/chla < 1000		X			-28.5 ± 0.1							
Porge	C/N > 15		$\delta^{13}C$: POC/chla < 100 ; N/C : mean of Cirès to Landes		X			-26.5 ± 1.1			0.050 ± 0.007				
Cirès / Renet / Milieu / Lanton / Tagon	C/N > 15 and chla < 1		POC/chla < 1000 and POC% > 10		X			-28.5 ± 0.5			0.053 ± 0.013				
Leyre	C/N > 15 and chla < 1		POC/Chla < 1000. $\delta^{13}C$ < 28.59 and POC% > 10		X			-28.3 ± 0.5			0.06 ± 0.005				
Landes	C/N > 12		POC/Chla < 600. $\delta^{13}C$ < -29.1		X			-29.1 ± 0.4			0.075 ± 0.002				
Adour	POC/chla > 3000		POC/chla < 200		X			-26.0 ± 0.9			0.099 ± 0.008				
Têt	C/N > 11.5	POC% < 4.25	PN% > 2. $\delta^{13}C$ < 26 and δ15N > 5	Measured			X	-26.0 ± 0.2	3.7 ± 0.6	12.2 ± 0.5	0.082 ± 0.002	-26.0 ± 0.6	6.7 ± 1.4	5.8 ± 1.4	0.180 ± 0.045
Aude	C/N > 12	Q7 > 70	PN% > 1 or 2 and C/N < 6				X	-28.1 ± 0.6	6.3 ± 0.1	15.3 ± 1.6	0.066 ± 0.007	-28.0 ± 0.7	4.7 ± 0.4	7.3 ± 1.0	0.139 ± 0.018
Orb	C/N > 10		PN% > 2. $\delta^{15}N$ > 4.06	Lower $\delta^{15}N$			X	-27.1 ± 0.4	3.7 ± 0.4	10.5 ± 0.3	0.095 ± 0.350				
Hérault	C/N > 12	Q > 45	PN% > 2				X	-27.7 ± 0.2	6.1 ± 0.7	13.7 ± 1.2	0.073 ± 0.007	-27.8 ± 0.4	4.7 ± 0.6	8.2 ± 1.5	0.124 ± 0.019
Rhône	C/N > 12	POC% < 1.25	C/N < 6.68 and $\delta^{15}N$ > 3.92				X	-26.4 ± 1.3	5.2 ± 1.0	17.0 ± 3.2	0.061 ± 0.012	-25.9 ± 0.4	3.1 ± 0.8	8.8 ± 3.1	0.119 ± 0.032

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Table 2 (continued)

River	Phytoplankton							WWTP's POM			
	$\delta^{13}C$ + equations		$\delta^{15}N$ + equations		C/N	N/C + equations		$\delta^{13}C$	$\delta^{15}N$	C/N	N/C
Seine	-32.8 ± 1.1		8.4 ± 1.7		7.4 ± 0.7	0.136 ± 0.012					
Orne	-31.4 ± 0.8		4.3 ± 0.8		6.6 ± 1.3	0.141 ± 0.010					
Rance	[-31.4;-25;6] ± 1.7	5.7x10^{-4}×[chla+phaeo]²-0.04×[chla+phaeo]-30.6	[4.7;11.4] ± 0.7	-0.28×[NO_3^-]+12.7	6.2 ± 0.4	0.161 ± 0.010					
Elorn	-27.4 ± 0.3		6.9 ± 0.5		10.0 ± 0.9	0.101 ± 0.007					
Aulne	-28.1 ± 0.2		8.6 ± 0.2		8.2 ± 0.2	0.122 ± 0.003					
Loire	[-30.6;-25.0] ± 0.9	5x10^{-4}×[chla+phaeo]²-0.02[chla+phaeo]-0.39[chla/phaeo]-27.9	[3.0;10.4] ± 1.2	4.2x10^{-4}[chla]²-0.08[chla]+8.2	7.2 ± 0.6	0.140 ± 0.011					
Sèvre Niortaise	[-35.7;-29.2] ± 1.0	-258×exp([chla+phaeo]²/16055)-0.15×[temp]+229				[0.106;0.145] ± 0.006	2.9x10^{-3}×[chla+phaeo] + 0.1				
Charente	-30.8 ± 0.03		7.5 ± 1.6		6.6 ± 0.3	0.152 ± 0.006					
Seudre	-33.3 ± 0.1										
Porge	-33.6 ± 0.4					0.128 ± 0.008					
Cirès / Renet / Milieu / Lanton / Tagon	-34.9 ± 0.4					0.133 ± 0.006					
Leyre	-30.1 ± 0.3					0.140 ± 0.016					
Landes	-29.9 ± 0.3					0.112 ± 0.010					
Adour	-28.2 ± 0.6					0.111 ± 0.010					
Têt	[-29.7;-27.8] ± 0.6	-5.2×10^{-3}[temp]²+0.08×[temp]-27.5	[5.3;13.3] ± 1.8	5.53×[temp]-5.5	5.6 ± 0.7	0.181 ± 0.021		-26.3 ± 0.1	-0.7 ± 0.1	6.3 ± 0.3	0.160 ± 0.017
Aude	[-32.6;-27.8] ± 0.6	-0.21×[temp]-26.5	[5.2;10.6] ± 1.6	-1.13×$\delta^{13}C$-26.2	5.0 ± 0.8	0.205 ± 0.033					
Orb	[-30.7;-23.4] ± 0.6	-0.19×[temp]-26.0	[4.9;8.4] ± 0.6	8.44-(3.63×(conduc-505))/(conduc-111)	4.8 ± 0.9	0.213 ± 0.039		-27.1 ± 0.4	1.9 ± 1.9	3.7 ± 3.7	0.270 ± 0.270
Hérault	[-31.5;-27.5] ± 1.0	-0.19×[temp]-26.0	[6.3;10;9] ± 1.3	3.6x10^{-2}×[temp]²-1.15×[temp]+14.6	5.0 ± 0.7	0.203 ± 0.031					
Rhône	-27.8 ± 1.2		5.6 ± 0.8		5.5 ± 0.8	0.180 ± 0.030					

2.4. Quantification of POM composition

POM composition was quantified using a Bayesian mixing model (‘*simmr*’ R package version 0.4.5, Govan and Parnell, 2023) which solves the equations system based on bulk and source POM elemental and isotopic signatures. Mixing models were computed for each sampling date of each river (Tab. 1), using carbon ($\delta^{13}C$ and N/C ratio, Eq. 4, 7, 8), nitrogen ($\delta^{15}N$ and C/N ratio, Eq. 5, 6, 8), and/or a combination of three ($\delta^{13}C$, $\delta^{15}N$ and N/C ratio, Eq. 4, 5, 7, 8) tracers. From the three mixing models performed for each sampling date and river (carbon, nitrogen or mixed), one model was selected as the best estimation of bulk POM data. It should be noted that N/C and C/N ratios give information on the mixing of C and N, respectively (Perdue and Koprivnjak, 2007). We used at least the same number of equations as unknowns (sources) to avoid running underdetermined models that result in large uncertainty in model outputs(Phillips et al., 2014). Equations of the models were:

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$$\delta^{13}C_{mixture} = x_1\ \delta^{13}C_{source\ 1} + x_2\ \delta^{13}C_{source\ 2} + x_3\ \delta^{13}C_{source\ 3} + x_4\ \delta^{13}C_{source\ 4} \qquad \text{(Eq. 4)}$$

$$\delta^{15}N_{mixture} = x_1\ \delta^{15}N_{source\ 1} + x_2\ \delta^{15}N_{source\ 2} + x_3\ \delta^{15}N_{source\ 3} + x_4\ \delta^{15}N_{source\ 4} \qquad \text{(Eq. 5)}$$

$$C/N_{mixture} = x_1\ C/N_{source\ 1} + x_2\ C/N_{source\ 2} + x_3\ C/N_{source\ 3} + x_4\ C/N_{source\ 4} \qquad \text{(Eq. 6)}$$

$$N/C_{mixture} = x_1\ N/C_{source\ 1} + x_2\ N/C_{source\ 2} + x_3\ N/C_{source\ 3} + x_4\ N/C_{source\ 4} \qquad \text{(Eq. 7)}$$

$$x_1 + x_2 + x_3 + x_4 = 1 \qquad \text{(Eq. 8)}$$

As there was no *a priori* knowledge of sources contributions to the POM mixture, the models were set with an uninformative prior (1, 1, 1, 1) following a Dirichlet distribution (all sources have an equal probability to contribute to the mix; Phillips et al., 2014). Model runs were set following the recommendations of Phillips et al. (2014). Models outputs were evaluated with Gelman-Rubin diagnostic (verification of chain convergence) and predictive distributions to ensure the good fit of the models to the observed data. Models outputs are given as medians. Absolute uncertainties for the models varied from 1 to 18 % (range of average for each river) with an overall average of 8 % (all models).

2.5. Forcings at local and multi-systems scales

Environmental forcings driving POM composition were determined using redundancy analysis (RDA; 'dudi.pca' and 'pcaiv' functions; R package {ade4} version 1.7-19). RDA summarizes multiple linear regressions between the response variable (POM composition: mixing model outputs) and a set of explanatory variables (environmental forcings) to assess causality links (Legendre et al., 2011). RDAs were performed at single-river and multi-river scales. Regarding the multi-rivers scale, the annual mean POM composition of each river was used to determine the drivers of spatial (i.e., between-rivers) variations of POM composition.

The proxies of the environmental forcings were chosen to directly or indirectly reflect processes that occur in the river and the adjacent ecosystems (e.g., primary production, soil leaching or WWTP's discharge) influencing POM source inputs and isotopic values. To homogenize the data sets for running the single-river RDAs, the same combination of twelve proxies for environmental forcings was used for each river: SPM, chlorophyll *a*, phaeopigments, temperature, daily river flow, pH, ammonium, nitrates, phosphates, irradiance, zonal and meridional wind. For the multi-river RDA, environmental proxies were selected to reflect processes occurring at large spatial scales and in the river basin. Hence, a new combination of sixteen proxies was used: river flow, conductivity, air temperature, precipitations, zonal and meridional wind, artificial, agricultural, forest and natural and wetlands surface areas, net soil erosion, organic carbon content in the soil, river length, basin surface area, latitude, longitude. From this initial list of proxies, some were removed to limit the auto-correlation (use of the Variance Inflation Factor, Borcard et al., 2011) and to improve the adjusted R^2 of each RDA analysis.

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2.6. Typology of systems

Rivers were classified based on POM composition and its temporal dynamics by performing a regionalization analysis as in Liénart et al. (2018) (Fig. A1). This method based on multivariate cluster analysis allows to consider the temporal (seasonal) variations specific to each river in addition to the spatial (between-rivers) component. The regionalization analysis was based on POM composition data (i.e., proportions of sources) computed for each river and each month. When more than twelve months were available (bi-monthly sampling or more years), a standard year of twelve months was chosen (averaged by month if fortnight dates). (Souissi et al., 2000)

A contingency matrix (rivers, sources, months) was created from monthly values of source contributions (i.e., mixing model outputs). For each month, a dendrogram was performed and ten cut-off levels were considered. Then, for each cut-off level, similarities between stations were identified within the twelve-monthly dendrograms. Ultimately, global similarities between rivers were computed using a fuzzy cluster that returns probabilities of membership of each river to each cluster type. The best number of river types, i.e., river typology, was determined considering the best Dunn coefficient (Dunn, 1974) and Silhouette score (Rousseeuw, 1987).

3. Results

Hereafter, four rivers were selected and considered as representative of each type of studied river (see section 3.4). Thus, most of the results are illustrated using these four rivers. Graphs of all the other rivers are reported in the supplementary material.

3.1. Contrasted seasonalities in river characteristics

As stated in section 2.1, the 23 studied rivers encompassed large gradients of environmental characteristics, as illustrated by the lowest and highest annual means of river flow (0.3 and 1572 m^3/s; Lanton and Rhône Rivers), water temperature (12.3 to 17.1 °C; Cirès and Têt Rivers), SPM (2.7 and 40.9 mg/l; Cirès and Rhône River), POC (0.3 and 5.1 mg/l; Hérault and Loire Rivers) and chlorophyll *a* (0.4 to 57.1 µg/l; Cirès and Rance Rivers) concentrations as well as POC/chl *a* (199 and 6444 g/g; Loire and Leyre Rivers) and C/N (5.9 and 20.3 mol/mol; Têt and Lanton Rivers) ratios; this was less contrasted among rivers for $\delta^{13}C$ (-30.2 and -26.2 ‰; Sèvre and Têt Rivers) and especially $\delta^{15}N$ (4.0 and 8.0 ‰; Leyre and Rance Rivers) (Fig. 2, A2).

As generally observed in rivers from mid-latitude, studied rivers exhibited clear seasonal patterns in water temperature with lower and higher values in winter and summer, respectively. However, such clear seasonal patterns were not always recorded for all the parameters, as there were contrasted patterns of seasonal variability among rivers. Indeed, the seasonal variability of river flow was quite smooth (e.g., the Rance and Charente Rivers) with a higher flow in winter/spring and lower flow in summer/fall for some rivers, whereas it was highly pulsed for some others with constant low levels marked by short and strong floods (e.g., 53m^3/s in mean

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but 1169m^3/s in flood time for the Hérault River) (Fig. 2). Overall, one can distinguish rivers that are characterized by high concentrations of chlorophyll *a* and clear seasonal patterns of most parameters (e.g., 53 µg/l of chlorophyll *a* in mean ranging from 3 to 135 µg/l in the Rance River) from rivers characterized by low concentrations of chlorophyll *a*, high POC/chl *a* and low seasonal variability for most of the parameters (e.g., 1.1 µg/l of chlorophyll *a* in mean ranging from 0.7 to 1.7 µg/l in the Milieu River) and from rivers that are characterized by high seasonal variability of most parameters but without a clear seasonal pattern (e.g., Hérault River). Other rivers exhibited intermediate behavior (e.g., Charente River) (Fig. 2, A2). Usually, Rance-like rivers exhibited high concentrations of chlorophyll *a* in spring/summer associated with POC/chl *a* ratio lower than 200 g/g, C/N ratio lower than 8 mol/mol and low δ^{13}C (down to -31 ‰ or -33 ‰; e.g., Seine River, Fig. A2). In contrast, Milieu-like rivers exhibited high POC/chl *a* (> ~ 700 g/g) and C/N ratio (> 15 mol/mol) and quite constant δ^{13}C (~-29 – -28 ‰) all year round (e.g., Cirès and Renet Rivers). These rivers are tributaries of the Arcachon Lagoon. Hérault-like rivers flowing into the Mediterranean Sea exhibited highly and suddenly variable C/N ratios (4 – 17 mol/mol), δ^{13}C (~-33 – -26 ‰) and δ^{15}N (~2 – 12 ‰) (e.g., Aude and Orb Rivers; Fig. A2).

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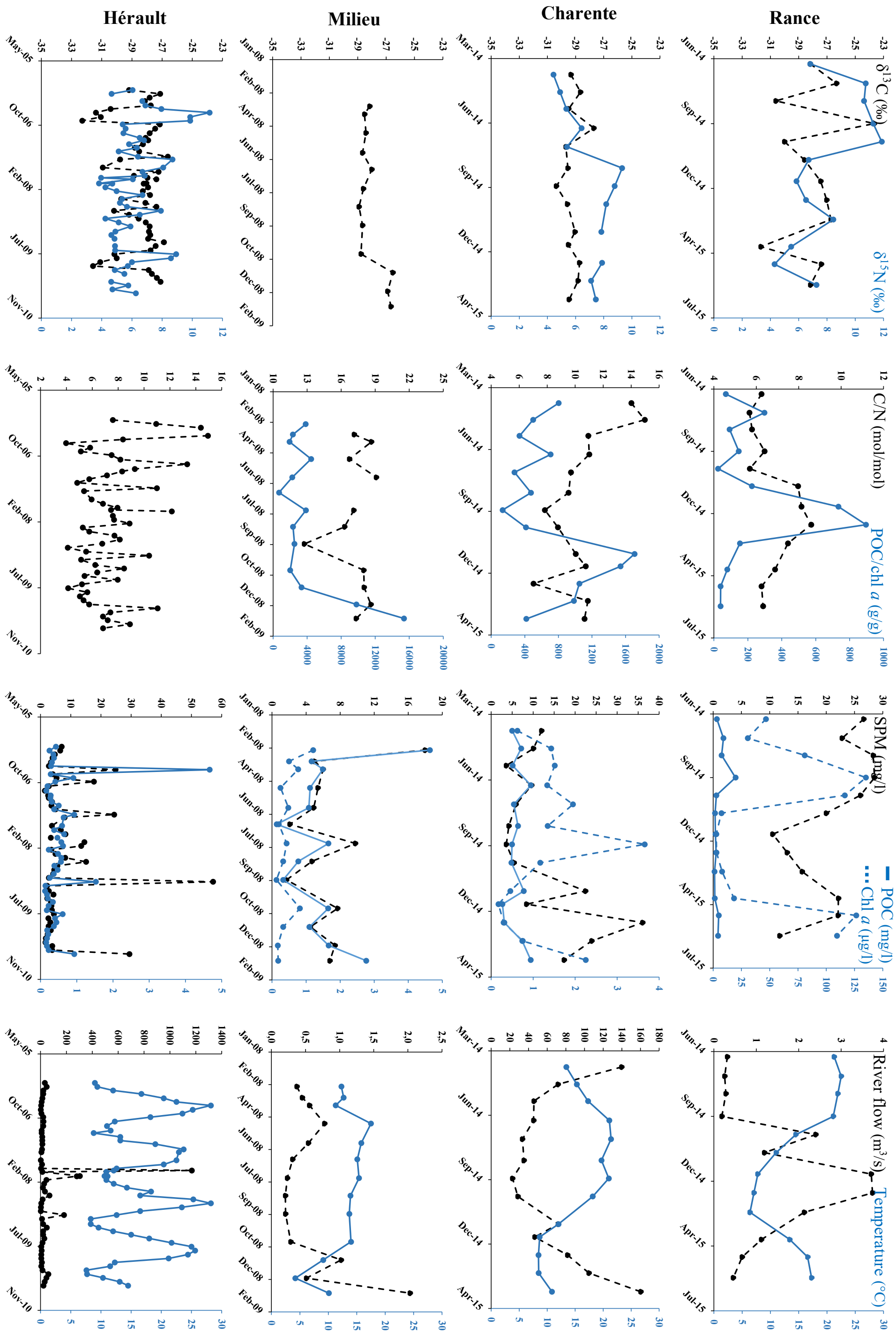

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Figure 2 Temporal variations of matter characteristics for representative rivers along the studied periods for $\delta^{13}C$ (left axis; black dotted line) and $\delta^{15}N$ (right axis; blue line) (first column); C/N (left axis; black dotted line) and POC/chl a(right axis; blue line) ratios (second column); SPM(left axis; black dotted line), POC (right axis; blue line) and chl *a* (right axis; blue dotted line) concentrations (third column) and river flow (left axis; black dotted line) and temperature (right axis; blue line) (fourth column).

3.2. Elemental and isotopic signatures of POM sources

Elemental and isotopic signatures of phytoplankton were estimated for each of the twenty-three rivers (Tab. 2, Fig. 3 and A3). Most of them (all of them for the C/N ratio) were found constant over time. Their annual mean values varied between -34.9 ‰ (some tributaries of the Arcachon Lagoon) and -27.4 ‰ (Elorn River) for $\delta^{13}C$, between 4.3 ‰ (Elorn River) and 8.6 ‰ (Aulne River) for $\delta^{15}N$ and between 4.8 mol/mol (Orb River) and 10.0 mol/mol (Elorn River) for the C/N ratio. Some of them varied over time along with pigment concentration and ratio or with temperature for $\delta^{13}C$, and with pigment concentration, nitrate concentration, temperature, $\delta^{13}C$ or conductivity for $\delta^{15}N$ (Tab. 2). The range of temporal variability was usually 4-6 ‰ for $\delta^{13}C$ and $\delta^{15}N$. Overall, phytoplankton signatures are comprised between -35.6 and -23.8 ‰ for the $\delta^{13}C$ and between 3.0 and 13.2 ‰ for the $\delta^{15}N$.

All other signatures were found constant over time (Tab. 2 and A2, Fig. 3 and A3) but may differ between rivers. Signatures mean annual values of labile terrestrial POM were comprised between -29.1 and -26.0 ‰ for the $\delta^{13}C$, between 3.7 and 6.6 ‰ for the $\delta^{15}N$ and between 8.8 and 17.0 mol/mol for the C/N ratio. Signatures mean annual values of refractory terrestrial POM were comprised between -28.0 and -25.9 ‰ for the $\delta^{13}C$, between 3.1 and 6.7 ‰ for the $\delta^{15}N$ and between 5.8 and 8.8 mol/mol for the C/N ratio. Signatures mean annual values of sewage POM were -27.1 and -26.3 ‰ for $\delta^{13}C$, 1.9 and -0.7 ‰ for $\delta^{15}N$ and 3.7 and 6.3 mol/mol for C/N ratio for Orb and Têt Rivers, respectively.

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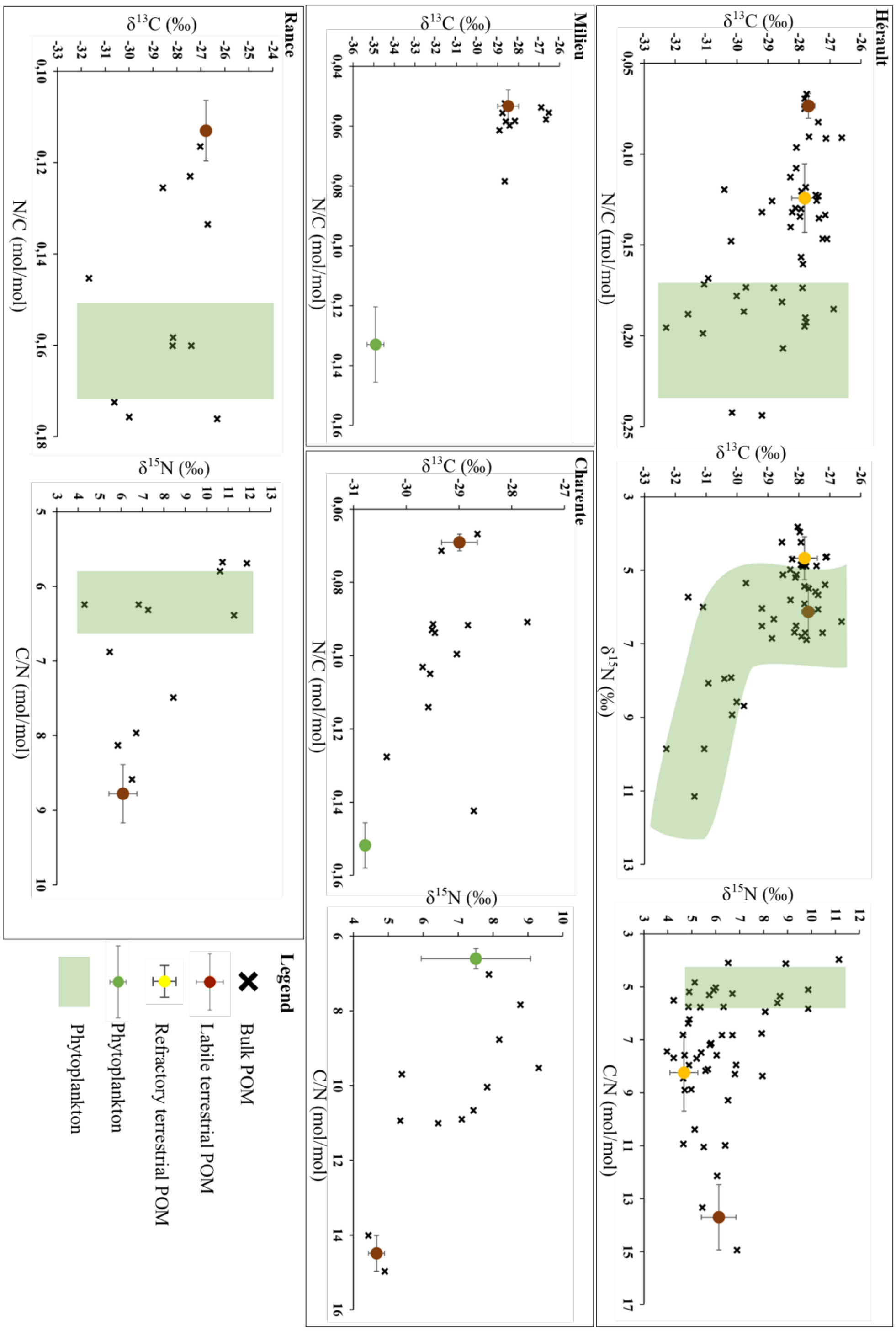

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Figure 3 $\delta^{13}C$, $\delta^{15}N$, N/C or C/N values of bulk POM (black crosses) and sources. The latter are presented as closed circles (average) and bars (standard deviation) when the signatures were constant over time and by colored area when at least one of the proxies was variable over time (see Table 2). This colored area corresponds to the dispersion of the values including their uncertainties.

3.3.Dynamics of particulate organic matter composition

Particulate organic matter composition resulting from mixing models outputs is presented hereafter, for each river, as the relative contribution of each source to the POM pool (Fig. 4). Among rivers whose POM is composed of only two sources (terrestrial POM and phytoplankton), one can distinguish rivers with terrestrial-dominated POM (e.g., Milieu River: terrestrial POM accounted for 94 ± 3 % of the mixture) to rivers of intermediate POM composition (e.g., Charente and Rance Rivers where phytoplankton accounted for 34 ± 10 % and 62 ± 10 % of the mixture, respectively). All these rivers flow in the English Channel and the Atlantic Ocean. The rivers whose POM is composed of three or four sources flow in the Mediterranean Sea. In these rivers, terrestrial POM is present as refractory and labile materials. The contribution of labile terrestrial POM ranged between 16 ± 15 % (Têt River) and 46 ± 21 % (Orb River), and of refractory terrestrial POM between 21 ± 9 % (Rhône River) and 39 ± 15 % (Aude River). The contribution of phytoplankton ranged between 34 ± 15 % (Aude River) and 51 ± 30 % (Hérault River) for the Mediterranean rivers. The fourth source of POM was WWTP's POM. It was identified as a source in the Orb and Têt Rivers and accounted for 15 ± 6 % and 10 ± 7 % in these two rivers respectively. Regarding temporal variations of POM composition, some rivers exhibited clear seasonal patterns whereas others revealed a homogeneous composition over the annual cycle (Fig. 4). The rivers where POM was highly dominated by terrestrial POM (Seudre, Cirès, Renet, Lanton, Milieu, Tagon, Leyre Rivers) showed almost no seasonal variability. In contrast, some rivers like the Rance, the Elorn or the Aulne River showed a clear seasonal pattern with the dominance of terrestrial material in winter and phytoplankton in summer. At last, other rivers exhibited less clear (e.g., Landes, Porge, Charente Rivers) or even no clear seasonal pattern but a quite stochastic variability over the annual cycle (e.g., Sèvre, Adour, Aude, Orb).

It should be noted that the above is valid for carbon and mixed as well as nitrogen models (cf. Tab. 2; Fig. 4 and A4).

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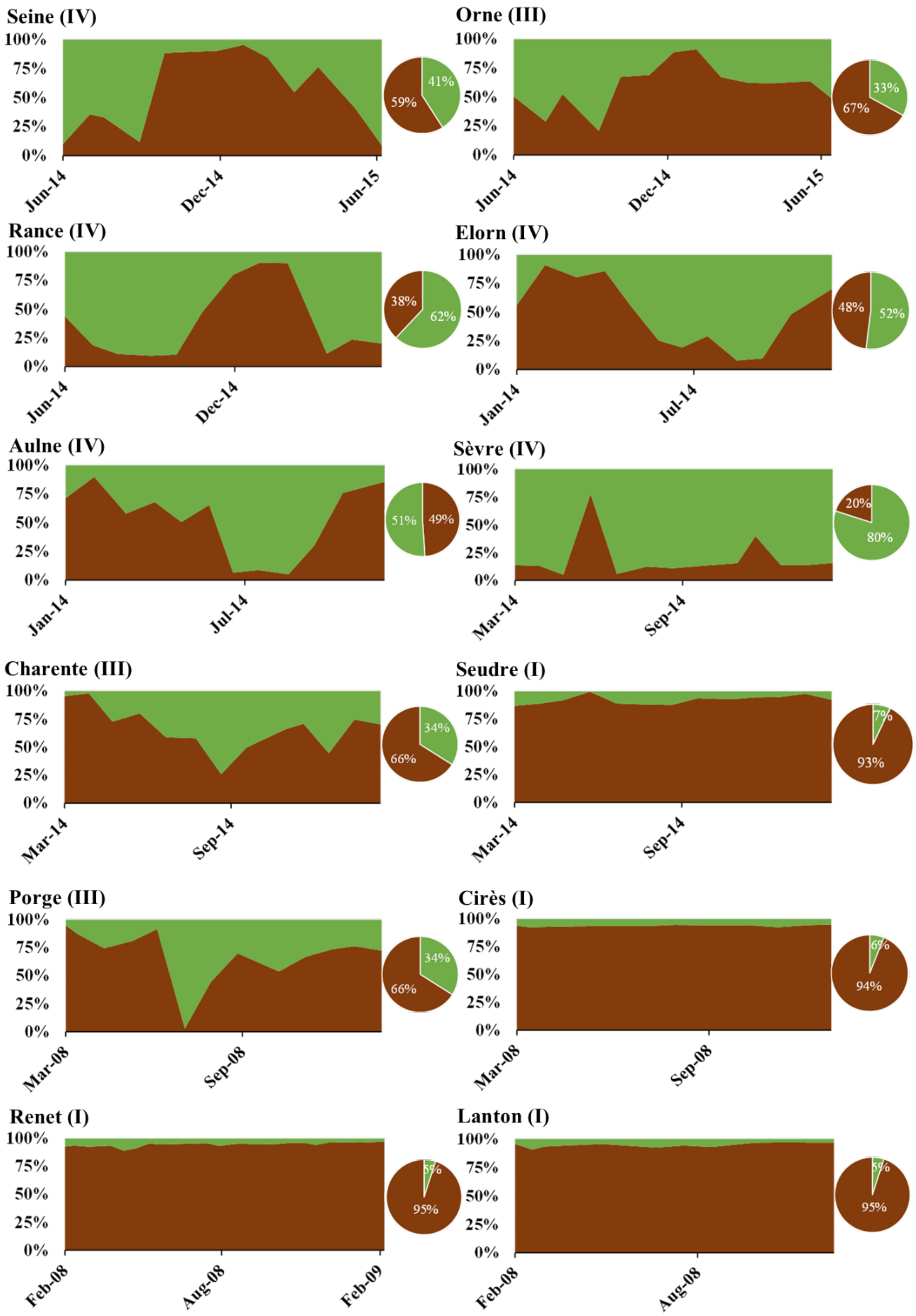

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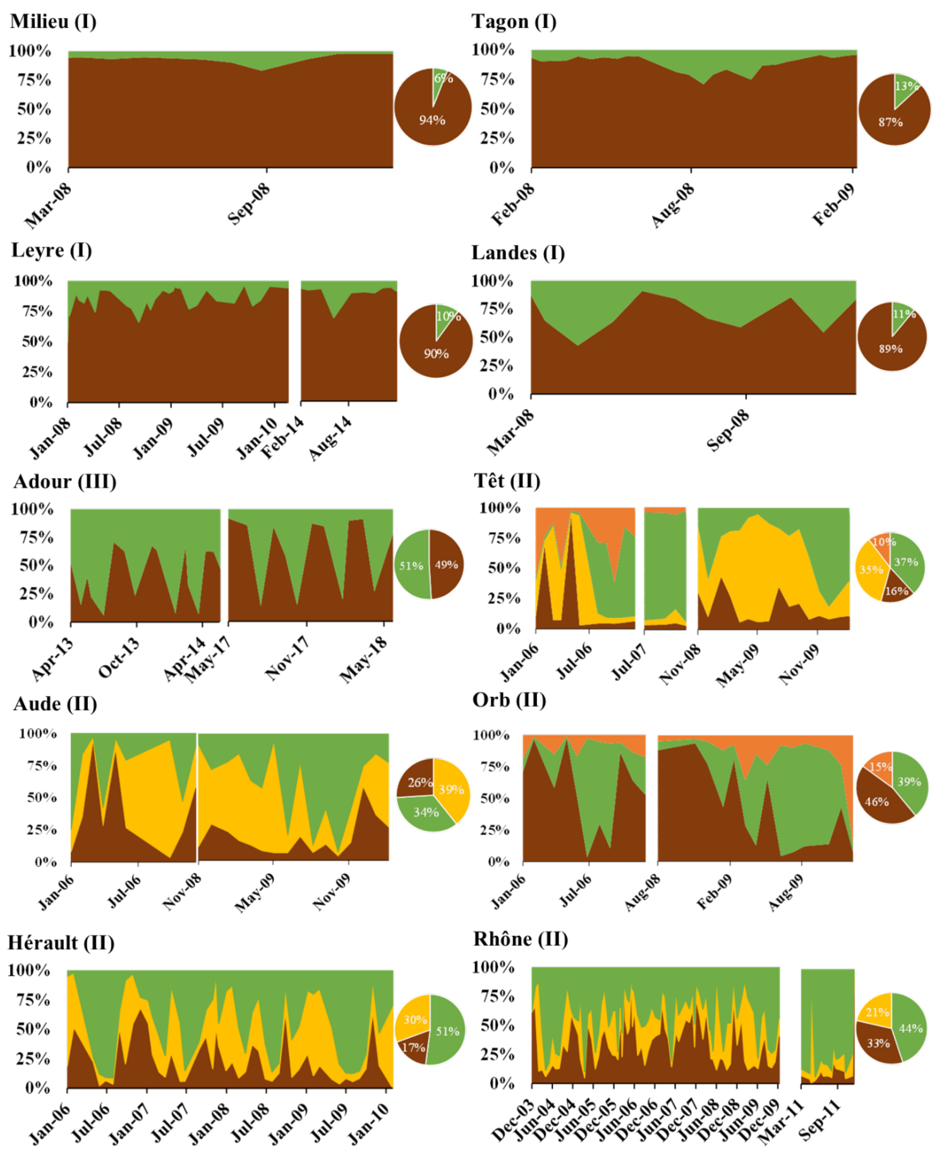

Figure 4 Temporal dynamic (rectangle graphs) and (inter-)annual mean (pie charts) of POC source proportions. Sources are phytoplankton (green), labile terrestrial material (brown), refractory terrestrial material (yellow) and anthropogenic POM (orange).

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3.4. Typology of rivers

Four types of rivers were determined by the regionalization analysis based on river POM composition and its temporal dynamics (Fig. 5). The seven rivers (Renet, Cirès, Lanton, Milieu, Seudre, Tagon and Leyre River) mainly belonging to Type I are characterized by terrestrial-dominated POM and no/low seasonality. Six of them are small streams/rivers flowing to the Arcachon Lagoon. The five rivers (Aude, Hérault, Têt, Rhône and Orb River) mainly belonging to Type II are characterized by the co-occurrence of labile and refractory terrestrial POM and large temporal variability but, except for the Hérault River, without a clear seasonal pattern. They all flow to the Mediterranean Sea. The five rivers (Porge, Adour, Charente, Orne and Landes River) mainly belonging to Type III are composed of phytoplankton and terrestrial POM, and exhibit moderate seasonality. Type III is clearly an intermediary between Type I and Type IV. These five rivers flow to the Atlantic Ocean or the English Channel. Among the seven rivers flowing to the Arcachon Lagoon, the two that mainly belong to Type III are man-managed streams and flow through lakes, contrary to the six other ones, which mainly belong to Type I and are natural streams that do not flow through lakes. Finally, the six rivers (Rance, Elorn, Aulne, Loire, Seine and Sèvre River) mainly belonging to Type IV are composed of phytoplankton and terrestrial POM, and exhibit high seasonality. These six rivers flow to the Atlantic Ocean or the English Channel.

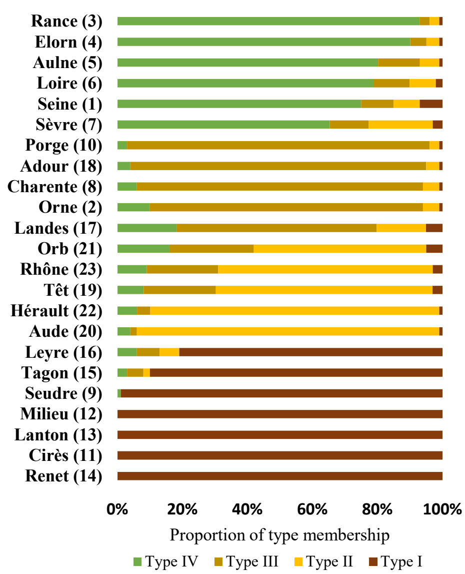

Figure 5 Typology of rivers following a hierarchical cluster analysis on POM source proportions. The percentages of membership for each type attributed to each river are shown.

3.5. Environmental forcings driving POM composition

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One redundancy analysis was performed for each river to relate environmental parameters, considered as proxies of drivers, to the POM composition, i.e., to assess the drivers of the temporal variability of POM composition for each river (Fig. 6 and A5). It should be kept in mind that the POC or PN concentration of each source was used for these analyses and not the relative proportion of the sources. In type-I rivers, i.e., rivers characterized by terrestrial-dominated POM and no/low seasonality, terrestrial POM is usually linked to river flow and/or SPM concentration (e.g., Milieu River on Fig. 6, Leyre and Tagon Rivers in Fig. A5). However, this feature is not always clear since the POM of these rivers is always dominated by terrestrial material, almost whatever the environmental conditions are. In type-II rivers, i.e., rivers characterized by the co-occurrence of labile and refractory terrestrial POM and large temporal variability, phytoplankton POM is usually positively linked to temperature and negatively linked to river flow, whereas labile and refractory terrestrial POM is positively linked to SPM and/or river flow. Interestingly, labile terrestrial POM is usually better linked to river flow and refractory terrestrial POM to SPM (e.g., Hérault River in Fig. 6 and Rhône River in Fig. A5). In the Têt River, anthropogenic POM was linked to nitrate concentration (Fig. A5). In rivers characterized by phytoplankton and terrestrial-POM composition with moderate (Type III) or high (Type IV) seasonality, terrestrial POM was almost always positively linked to river flow and/or SPM concentration while phytoplankton was usually linked with chl *a* concentration (e.g., Charente and Rance River on Fig. 6, Landes and seine River on Fig. A5).

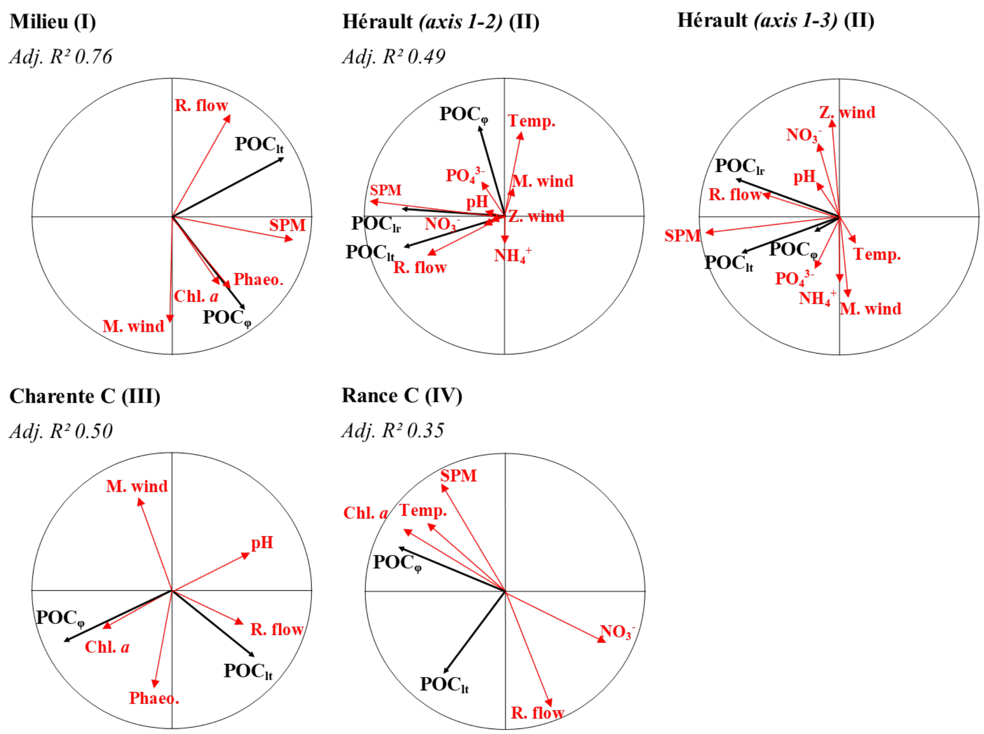

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Figure 6 Redundancy analyses (correlation circles) of rivers standing for each type of river. Black arrows represent explained variables (concentration of POC sources) and red arrows represent explaining variables (environmental variables). River types are recalled (Roman numerals). POC_{lt} = Labile terrestrial POC; POC_{rt} = Refractory terrestrial POC; POC_{φ} = Phytoplankton POC; Chl a = chlorophyll a; Phaeo. = phaeopigments; M. wind = meridional wind; Z. wind = zonal wind; R. flow = river flow; Temp. = temperature; Irrad. = Irradiance; NH_4^+ = ammonium; NO_3^- = nitrate; PO_4^{3-} = phosphates ; Adj. R^2 = adjusted R^2.

At last, another RDA was performed gathering all rivers to relate environmental parameters to the mean annual POM composition at the multi-rivers scale (Fig. 7). As anthropogenic POM was only detected in two rivers (Orb, Têt), it was not included in the multi-rivers analysis to avoid analysis bias. At this scale, phytoplankton is strongly positively linked to agricultural surfaces, labile terrestrial material to soil erosion rate and soil organic carbon and refractory terrestrial material to river flow and water temperature.

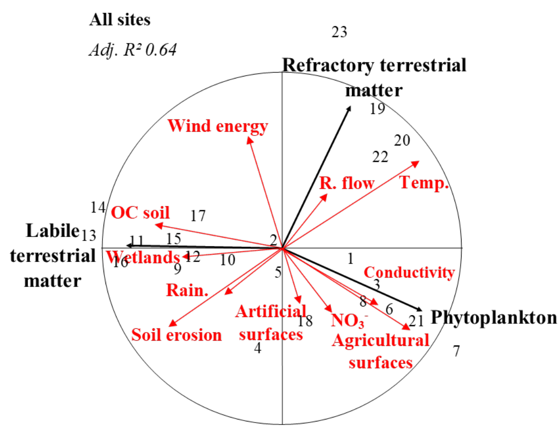

Figure 7 Multi-rivers redundancy analysis. Black arrows represent explained variables (relative proportions), red arrows represent explaining variables (environmental variables) and numbers are river identifiers (cf. Fig.1). R. flow = river flow; OC soil = percentages of organic carbon in soil; Soil erosion = soil erosion rate; Rain. = precipitations; NO_3^- = nitrate concentration ; Adj. R^2 = adjusted R^2.

4. Discussion

4.1. Bulk data and source signatures in temperate rivers

Over the 23 studied rivers, $\delta^{13}C$, $\delta^{15}N$ and C/N ratios of bulk POM ranged between -35.2 and -24.5 ‰, -0.3 and 12.6 ‰, and 3 and 23.4 mol/mol, respectively. This corresponds to usual values recorded for riverine POM over temperate systems, except for the lowest C/N ratios (Ferchiche et al., 2024; Kendall et al., 2001; Ogrinc et al., 2008).

In the present study, isotopic and elemental signatures of terrestrial POM and phytoplankton were determined from subsets of the bulk data sets following the approaches of Savoye et al. (2012), Liénart et al. (2017) and Ferchiche et al. (2025, 2024). It has the double advantage of 1) taking into account the reworking of terrestrial POM within the river and thus discriminating labile from refractory terrestrial POM, and 2) taking into account the variability of phytoplankton signature over time, due to differences in growth conditions (see below). Labile terrestrial POM mainly appears during high river flow (Fig. 6 and A5; Savoye et al., 2012) and is usually composed of riparian litter (e.g., Veyssy et al., 1998). In the studied rivers, $\delta^{13}C$, $\delta^{15}N$ and C/N ratio of labile terrestrial POM ranged between -28.9 ± 0.8 ‰ and -26 ± 0.9 ‰, 3.7 ± 0.6 ‰ and 6.6 ± 0.9 ‰, and 8.8 ± 0.4 and 17 ± 3.2 mol/mol, respectively. These values are very similar to values found in other temperate systems like the Gironde Estuary ($\delta^{13}C$ = -28.7 ± 0.9 ‰; Savoye et al., 2012), the Sava River ($\delta^{13}C$ = -28 ± 5 ‰; $\delta^{15}N$ = 5 ± 2 ‰; C/N = 33 ± 15 mol/mol; Ogrinc et al., 2008) or Taiwanese rivers ($\delta^{13}C$ = -26.6 ± 1.8 ‰; C/N = 31.1 ± 23.4 mol/mol; Hilton et al., 2010) and very similar to direct measurement of C3 plants ($\delta^{13}C$ = -28.1 ± 2.5 ‰; O'Leary, 1981 and references therein; $\delta^{13}C$ = -28 ± 1.3 ‰; $\delta^{15}N$ = 0.8 ± 2.9 ‰; C/N = 39.6 ± 25.7 mol/mol; Dubois et al., 2012; $\delta^{13}C$ = -27.9 ± 0.1 ‰; Fernandez et al., 2003). Refractory terrestrial POM is terrestrial POM that has undergone large reworking within river water, river sediment or even estuarine maximum turbidity zone (e.g., Etcheber et al., 2007; Veyssy et al., 1998). In the studied rivers where it was found, $\delta^{13}C$, $\delta^{15}N$ and C/N ratios of refractory terrestrial POM ranged between -28 ± 0.7 ‰ and -25.9 ± 0.4 ‰, 3.2 ± 0.8 ‰ and 6.7 ± 1.4 ‰, and 5.8 ± 1.4 and 8.8 ± 3.1 mol/mol, respectively. These values are very similar to those found in other systems like the Gironde Estuary (France) ($\delta^{13}C$ = -25.2 ± 0.3 ‰; $\delta^{15}N$ = 5.5 ± 0.4 ‰; C/N = 8.5 ± 0.8 mol/mol; Savoye et al., 2012), Taiwanese rivers ($\delta^{13}C$ = -23.6 ± 1.1 ‰; C/N = 6.5 ± 1.6 mol/mol; Hilton et al., 2010) and in the Pearl River (China) ($\delta^{13}C$: between -28.3 ± 0.8 ‰ and -21.7 ± 0.7 ‰; C/N: between 8.9 ± 1.1 and 17.9 ± 3.6 mol/mol; Yu et al., 2010).

Isotopic signatures of phytoplankton vary depending on biogeochemical conditions and processes like nutrient availability and utilization, growth rate and limitation (e.g., Fry, 1996; Liénart et al., 2017; Lowe et al., 2014; Miller et al., 2013; Savoye et al., 2003; Sigman et al., 2009; Yan et al., 2022) and can be estimated using measured environmental parameters (Ferchiche et al., 2024, 2025; Liénart et al., 2017; Savoye et al., 2012). For the seven rivers where phytoplankton isotopic signatures were found variable over time, phytoplankton $\delta^{13}C$ or $\delta^{15}N$ were correlated to: concentrations and ratio of chlorophyll *a* and phaeopigments, water temperature, nitrate concentration and/or conductivity (Tab. 2). Chlorophyll *a* and phaeopigments concentrations are direct proxies of phytoplankton fresh and degraded biomasses and are related to phytoplankton growth and decay, two processes that increase phytoplankton $\delta^{13}C$ (Golubkov et al., 2020; Michener and Kaufman, 2007 and references

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therein). Similar processes may explain phytoplankton-$\delta^{15}N$ increase with chlorophyll *a* increase. An increase in water temperature accelerates bio-mediated carbon remineralization processes bringing a lower $\delta^{13}C$ value than CO_2 coming from water-atmosphere equilibration and rock-leaching CO_2 (Polsenaere et al., 2013 and references therein). Consequently, phytoplankton $\delta^{13}C$ decreases as phytoplankton uses remineralized CO_2 and thus as water temperature increases. Phytoplankton $\delta^{15}N$ depends on N-nutrient origin and availability (Savoye et al., 2003 and references therein). Especially, it increases with nutrient concentration decrease (Sigman et al., 2009) as reported for the Rance River (Tab. 2). Water conductivity could be considered as a proxy of water mass and thus of nitrate origin. This may explain the relationship between phytoplankton $\delta^{15}N$ and water conductivity in the Orb River (Tab. 2).

In the studied rivers, phytoplankton $\delta^{13}C$, $\delta^{15}N$ and C/N ratio ranged between -34.9 ± 0.4 and -23.8 ± 0.6 ‰, 4.3 ± 0.8 and 13.2 ± 1.8 ‰, and 4.8 ± 0.9 and 10 ± 0.9 mol/mol, respectively. This is similar to values reported for the Loire River, another French river ($-30.6 \leq \delta^{13}C \leq -25.0$ ‰; $3.0 \leq \delta^{15}N \leq 10.4$ ‰; C/N = 7.2 ± 0.6 mol/mol: Ferchiche et al, 2024) but narrower ranges can be found in the literature. In the Sava River (Eastern Europe), phytoplankton signature was -30.4 ± 2.1 ‰, 5.0 ± 1.5 ‰ and 6.5 ± 1.5 mol/mol for $\delta^{13}C$, $\delta^{15}N$ and C/N ratio, respectively (Ogrinc et al., 2008), similar to that of Indian ($\delta^{13}C$ = -30.6 ± 1.7 ‰, $\delta^{15}N$ = 7.0 ± 2.3 ‰; Gawade et al., 2018) and Texan ($\delta^{13}C$ = -31,4 ‰; Lebreton et al., 2016) rivers. Lower $\delta^{13}C$ values (≤ -32 ‰) were also found (Finlay et al., 2010; Hellings et al., 1999; Sato et al., 2006; Savoye et al., 2012). However, values of elemental and isotopic ratios for riverine phytoplankton are scarce in the literature. Indeed, it is not easy to estimate phytoplankton signature since it cannot be separated from other particles. Thus, literature estimates may not be perfectly representative of the variability of phytoplankton isotopic signatures.

4.2. Watershed characteristic drive on spatial dynamics of POM composition

At the annual scale, we observed deep variations between studied rivers concerning the mean POC proportion of the different sources (5 ≤ phytoplankton ≤ 80 %; 17 ≤ labile terrestrial POC ≤ 95 %; 0 ≤ refractory terrestrial POC ≤ 39 %). Interestingly, phytoplankton proportion was highly correlated to the proportion of agriculture surface area (Fig. 7; R^2 = 0.59 or even 0.72 when Seudre River is not included in the statistics) and nitrate concentration (Fig. 7; R^2 = 0.41 when Seudre River is not included in the statistics). Such relationship between agriculture surface area and phytoplankton is well-known, as agricultural activities increase nutrient input to river bodies (Khan and Mohammad, 2014), leading to better conditions for phytoplankton growth (Dodds and Smith, 2016; Minaudo et al., 2015). Interestingly, the proportion of labile terrestrial matter was strongly linked to soil erosion and soil organic carbon content (Fig. 7) indicating a strong relationship between terrestrial matter in rivers and soil nature with undecomposed and fresh detrital matter (McCorkle et al., 2016).

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4.3. Temporal dynamics of POM composition and river typology

In aquatic systems, phytoplankton likely appears during spring and summer in favorable conditions, related to low discharge, high-temperature conditions and enough nutrients to support its growth, while in winter, high turbidity and low-temperature conditions limit its presence (Turner et al., 2022). Quantitative differences between rivers can be due to differences in nutrient availability, either because of anthropic mitigation (Minaudo et al., 2015), competition with other nutrient users (Descy et al., 2012; Minaudo et al., 2016) or sewage inputs (Codiga et al., 2022) in addition to agricultural inputs (see section 4.2). Terrestrial material likely appears during winter conditions, related to floods that transport great amounts of terrestrial material (Dalzell et al., 2007). Such a seasonal dichotomy between phytoplankton and terrestrial POM was clearly visible for most of the studied rivers (Fig. 4), especially for type-IV and type-III rivers, but even for some of those highly dominated by the labile terrestrial POM (e.g., Milieu and Tagon Rivers; Type-I rivers). This was illustrated by the relationships between phytoplankton POM and chlorophyll *a* concentration and/or temperature (as proxies of favorable conditions for phytoplankton production) on the one hand, and between labile terrestrial POM and river flow and/or SPM concentration on the other hand (Fig. 6 and A5). This dichotomy in POM composition was also reported in other similar studies (e.g., Kelso and Baker, 2020; Lu et al., 2016). In rivers where refractory terrestrial POM was present in addition to the labile one (type-II rivers), it was interesting to see that the refractory terrestrial POM was more related to SPM concentration than river flow and inversely for the labile terrestrial POM. This indicates that labile and refractory terrestrial POM were preferentially associated with direct river input and sediment resuspension, respectively. The origin of the refractory terrestrial POM may be fossil/bedrock/petrogenic OM (e.g., Copard et al., 2022; Hilton et al., 2010; Sun et al., 2021) brought by river flow (in quantity undetectable in the bulk POM using our tools) and then accumulated in the sediment, and/or labile terrestrial POM brought by the river flow and then accumulated and reworked/decayed in the sediment (e.g., Etcheber et al., 2007; Savoye et al., 2012).

Sewage POM was detected in two of the studied rivers but with different associated temporal dynamics. In the Têt River, because the former WWTP was dysfunctional, a new one replaced it in late 2007 (https://www.assainissement.developpement-durable.gouv.fr/pages/data/fiche-060966136002, last visit 10/09/24). This explains the shift in sewage POM between the two studied periods (2006-2007 versus 2008-2010 without anthropogenic POM). In the Orb River, sewage POM was detected throughout the studied periods. The WWTP is located only a few kilometers upstream of the sampling site and is large enough (220 000 inhabitant equivalent) compared to the river flow (annual mean: 23m^3/s) to make the sewage POM detectable in the bulk POM using $\delta^{15}N$. Such a result is quite common for urban rivers (e.g., Kelso and Baker, 2020).

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4.4. Originality of the study

The originality of the present study firstly lies in its approach. Even if C and N stable isotopes have been used for decades to investigate POM origins within river waters, the quantification of POM composition (i.e., the relative proportion of each source composing the POM) using mixing models, and especially Bayesian mixing models, is not so common. In addition, most of the previous studies either use literature data for phytoplankton isotopic signature (e.g., Zhang et al., 2021) or use lake or autochthonous POM as a proxy of phytoplankton (e.g., Kelso and Baker, 2020). Also, most of these studies use direct measurements of soil or plants to assess the isotopic signature of terrestrial POM whereas this material is able to rework within the water column or the sediment, which changes its elemental and isotopic values (e.g., Savoye et al., 2012). These approaches do not consider that isotopic signatures of phytoplankton and terrestrial material may change over time. In the present study, we used the approach developed by Savoye et al. (2012) in an estuary, Liénart et al. (2017) in coastal systems and Ferchiche et al. (2025, 2024) in a river to assess the elemental and isotopic signatures from subsets of bulk POM and when needed, empirical equations. This approach has the great advantage of 1) using signatures dedicated to the sampling area and 2) taking into account the potential variability of these signatures over time, i.e., depending on the environmental conditions for phytoplankton growth and taking into account its decay for phytoplankton and terrestrial POM. Especially, we were able to discriminate labile from refractory terrestrial POM in some rivers, as Savoye et al. (2012) in an estuary. Another great originality of the present study lies in the multi-systems approach: studying 23 rivers in a single study allowed the detection of four types of river functioning regarding the POM composition and its temporal dynamics. It also highlights the great influence of land use (agriculture) and characteristics (erosion, organic carbon content) on the POM composition of rivers. At last, using $\delta^{13}C$, $\delta^{15}N$ and C/N ratio all together allowed either to perform mixing models with up to four end-members or to study separately POC and PN composition. It showed that POC and PN display very similar compositions and dynamics in rivers.

5. Synthesis and perspectives

The present study proposes a comprehensive estimation of POM composition and its spatial and seasonal variability in temperate rivers. Thanks to the inclusion of twenty-three rivers, encompassing large gradients of environmental conditions under a temperate climate, a river typology is proposed based on the POM composition and its temporal dynamics. In type-I rivers, POM is dominated by labile terrestrial material all year long. This material is mainly associated with suspended particulate matter. Phytoplankton slightly contributes, especially during summertime. Type-II rivers are mainly characterized by the presence of both labile and refractory terrestrial material, in addition to phytoplankton. The temporal variability between these sources is high but the seasonality is not always pronounced even if phytoplankton and

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terrestrial POM can dominate the POM composition during summer and winter, respectively. Nevertheless, labile terrestrial POM is mainly related to river flow and refractory terrestrial POM to SPM, indicating the sedimentary origin of the latter. In type-III rivers, POM is composed of phytoplankton and labile terrestrial material. The seasonality of POM composition is not very pronounced even if the contribution of labile terrestrial POM is deeply related to river flows. Type III is an intermediary between type I and type IV. In type-IV rivers, POM is also composed of phytoplankton and labile terrestrial material but the seasonality of POM composition is very pronounced with a clear balance between high phytoplankton contribution in summer and high terrestrial contribution in winter. Labile terrestrial POM is deeply related to river flow. Beyond this typology, the main difference in POM composition between the studied rivers is that the phytoplankton contribution to the POM composition is related to the proportion of agricultural surface in the watershed and the contribution of labile terrestrial POM is related to soil erosion and organic carbon content in the watershed.

The originality of this study mainly lies in 1) the approach used to determine the elemental and isotopic signatures of POM sources, which allowed to discriminate labile from refractory terrestrial POM and to take into account, when any, the variability of the signatures over time, and 2) determining a typology of temperate rivers based on the POM composition and its temporal dynamics.

Overall, this study, which focuses on the River-Estuary Interface, brings meaningful information for the comprehension of C and N cycles along the LOAC and especially the behavior, dynamics and drivers of POM that leaves the river and enters the estuary.

From a methodological perspective, such a study could be strengthened by the use of non-exchangeable δ^2H as an additional tool to even better distinguish and quantify more sources in mixing models. This tool has been recently shown to be powerful for such purposes (Ferchiche et al., 2025). From a fundamental perspective, aggregating more datasets from other temperate rivers would allow testing the robustness of this typology and probably detecting additional types, but also datasets from polar and tropical rivers to perform an even more comprehensive study at a global climate scale. In addition, a similar study dedicated to the estuarine systems would even increase our comprehensive understanding of the origin and fate of POM along the Land-Ocean Aquatic Continuum by complementing the present study dedicated to the River-Estuary Interface and those of Liénart et al. (2017, 2018) dedicated to the coastal systems.

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Appendix

Toward a typology of river functioning: a comprehensive study of POM composition at multi-rivers scale

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Keywords : River-Estuary Interface; particulate organic matter; isotopes; multi-ecosystems study

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Table A1 Summary of data availability and origin (X means that the data were available; * means that the data were retrieved from the Naïades database; ** means that the data were retrieved from the Météo France database). n = number of sampling dates; SPM = Suspended Particulate Matter; POC or PN = Particulate Organic Carbon or Nitrogen; Chl *a* = Chlorophyll *a*; Phaeo = Phaeopigments.

River	Samplings					Parameters																				
	Dates	Periodicity	n	Latitude	Longitude	$\delta^{13}C$	$\delta^{15}N$	C/N ratio	SPM	POC	PN	Chl *a*	Phaeo	Water temperature	pH	Conductivity	NH_4^+	NO_2^-	NO_3^-	PO_4^{3-}	Flow	Rainfall	Air temperature	Wind direction	Wind intensity	Irradiance
Seine	06/2014 to 06/2015	monthly	13	49.306667	1.242500	X	X	X	X*	X	X	X	X	X*	X*	X*	X*	X*	X*	X*	X	X**	X**	X**	X**	
Orne	06/2014 to 06/2015	monthly	13	49.179722	-0.349167	X	X	X	X*	X	X	X	X	X*	X*	X*	X*	X*	X*	X*	X	X**	X**	X**	X**	X**
Rance	06/2014 to 05/2015	monthly	12	48.491667	-2.001389	X	X	X	X*	X	X	X	X	X*	X*	X*	X*	X*	X*	X*	X	X**	X**	X**	X**	X**
Elorn	01/2014 to 06/2015	monthly	17	48.450556	-4.248333	X	X	X	X*	X	X	X	X	X*	X*	X*	X*	X*	X*	X*	X	X**	X**	X**	X**	X**
Aulne	01/2014 to 06/2015	monthly	17	48.212778	-4.094444	X	X	X	X*	X	X	X	X	X*	X*	X*	X*	X*	X*	X*	X	X**	X**	X**	X**	X**
Loire	10/2009 to 07/2012	bi-monthly	67	47.392095	-0.860351	X	X	X	X*	X	X	X	X	X	X	X	X	X	X	X	X	X**	X**	X**	X**	X**
Sèvre niortaise	03/2014 to 03/2015	monthly	13	46.315348	-1.003891	X	X	X	X*	X	X	X	X	X*	X*	X*	X*	X*	X*	X*	X	X**	X**			
Charente	03/2014 to 03/2015	monthly	13	45.868056	-0.713056	X	X	X	X*	X	X	X	X	X*	X*	X*	X*	X*	X*		X	X**	X**	X**	X**	
Seudre	03/2014 to 09/2015	monthly	15	45.674027	-0.933123	X	X	X	X*	X	X	X	X	X*	X*	X*	X*	X*	X*	X*	X	X**	X**	X**	X**	X**
Porge	01/2008 to 02/2009	monthly	14	44.789868	-1.161181	X		X	X	X		X	X	X		X			X*		X	X**	X**	X**	X**	
Renet	02/2008 to 02/2009	bi-monthly	23	44.714466	-1.044013	X		X	X	X		X	X	X		X			X*		X	X**	X**	X**	X**	
Milieu	02/2008 to 02/2009	monthly	13	44.697326	-1.022532	X		X	X	X		X	X	X		X			X*		X	X**	X**	X**	X**	
Cirès	02/2008 to 02/2009	monthly	13	44.759820	-1.110657	X		X	X	X		X	X	X		X			X*		X	X**	X**	X**	X**	
Lanton	02/2008 to 02/2009	monthly	13	44.700283	-1.024385	X		X	X	X		X	X	X		X			X*		X	X**	X**	X**	X**	
Tagon	02/2008 to 02/2009	bi-monthly	26	44.659049	-0.989050	X		X	X	X		X	X	X		X			X*		X	X**	X**	X**	X**	
Landes	02/2008 to 02/2009	monthly	12	44.616912	-1.109066	X		X	X	X		X	X	X		X			X*		X	X**	X**	X**	X**	
Leyre	02/2008 to 02/2015	bi-monthly or monthly	59	44.626389	-0.996111	X	X	X	X*	X	X	X	X	X	X*	X*	X*	X*	X*	X*	X	X**	X**	X**	X**	
Adour	04/2013 to 05/2018	monthly	24	43.498880	-1.294899	X	X	X	X	X	X	X	X	X			X	X	X		X	X**	X**	X**	X**	X**
Têt	01/2006 to 05/2010	monthly	52	42.713704	2.993488	X	X	X	X	X	X			X	X	X	X*	X*	X*	X*	X	X**	X**	X**	X**	
Aude	01/2006 to 05/2010	monthly	52	43.244281	3.152733	X	X	X	X	X	X			X	X	X	X*	X*	X*	X*	X	X**	X**	X**	X**	X**
Orb	01/2006 to 05/2010	monthly	52	43.285004	3.281278	X	X	X	X	X	X			X	X	X	X*	X*	X*	X*	X	X**	X**			
Hérault	01/2006 to 05/2010	monthly	52	43.359415	3.435398	X	X	X	X	X	X			X	X	X	X*	X*	X*	X*	X	X**	X**	X**	X**	
Rhône	12/2003 to 01/2011	monthly	105	43.678724	4.621188	X	X	X	X	X	X	X	X	X	X	X	X*	X*	X*	X*	X	X**	X**	X**	X**	X**

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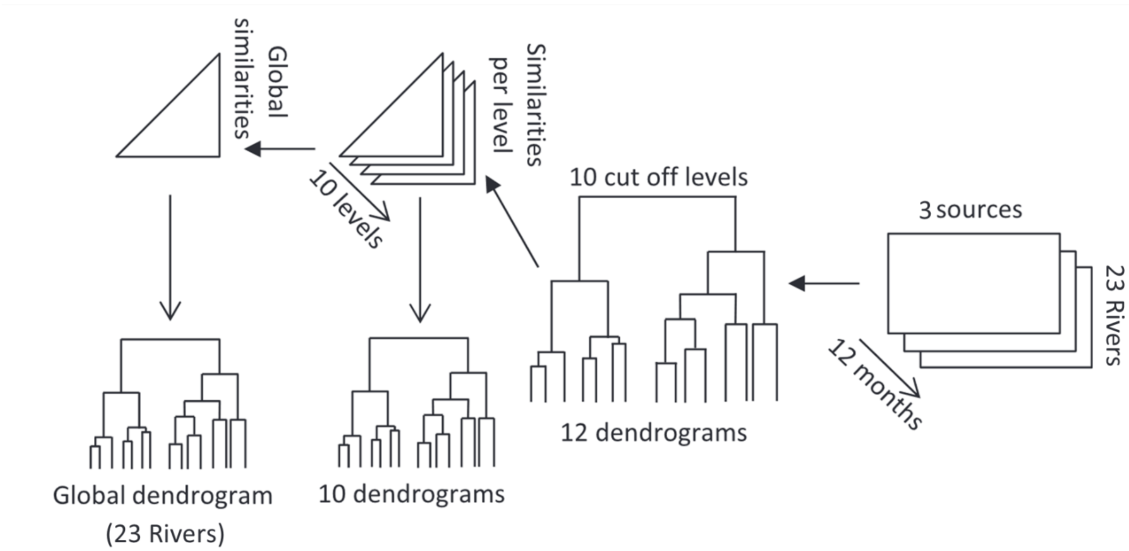

Figure A1 Diagram detailing the regionalization method, adapted from Souissi et al. (2000).

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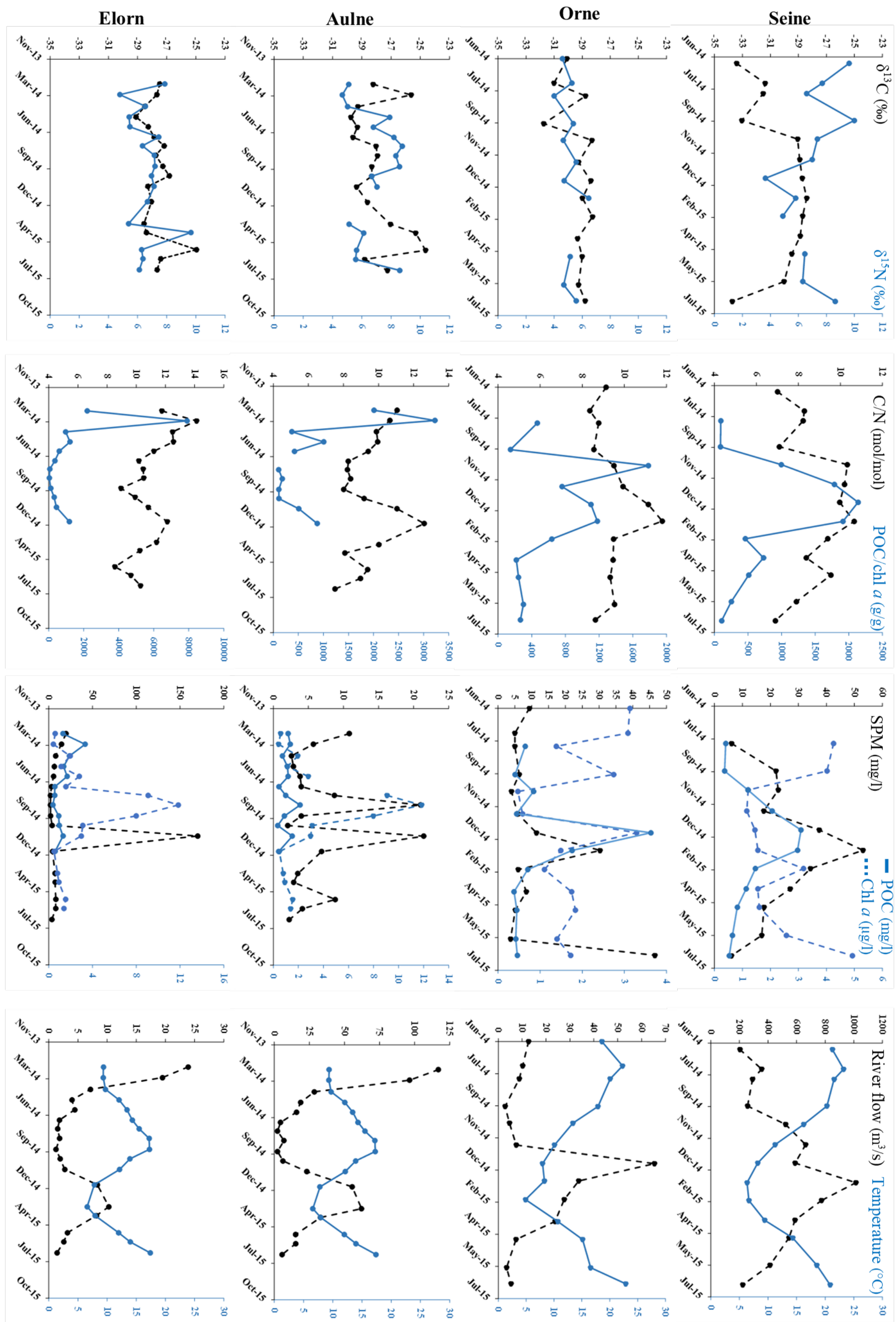

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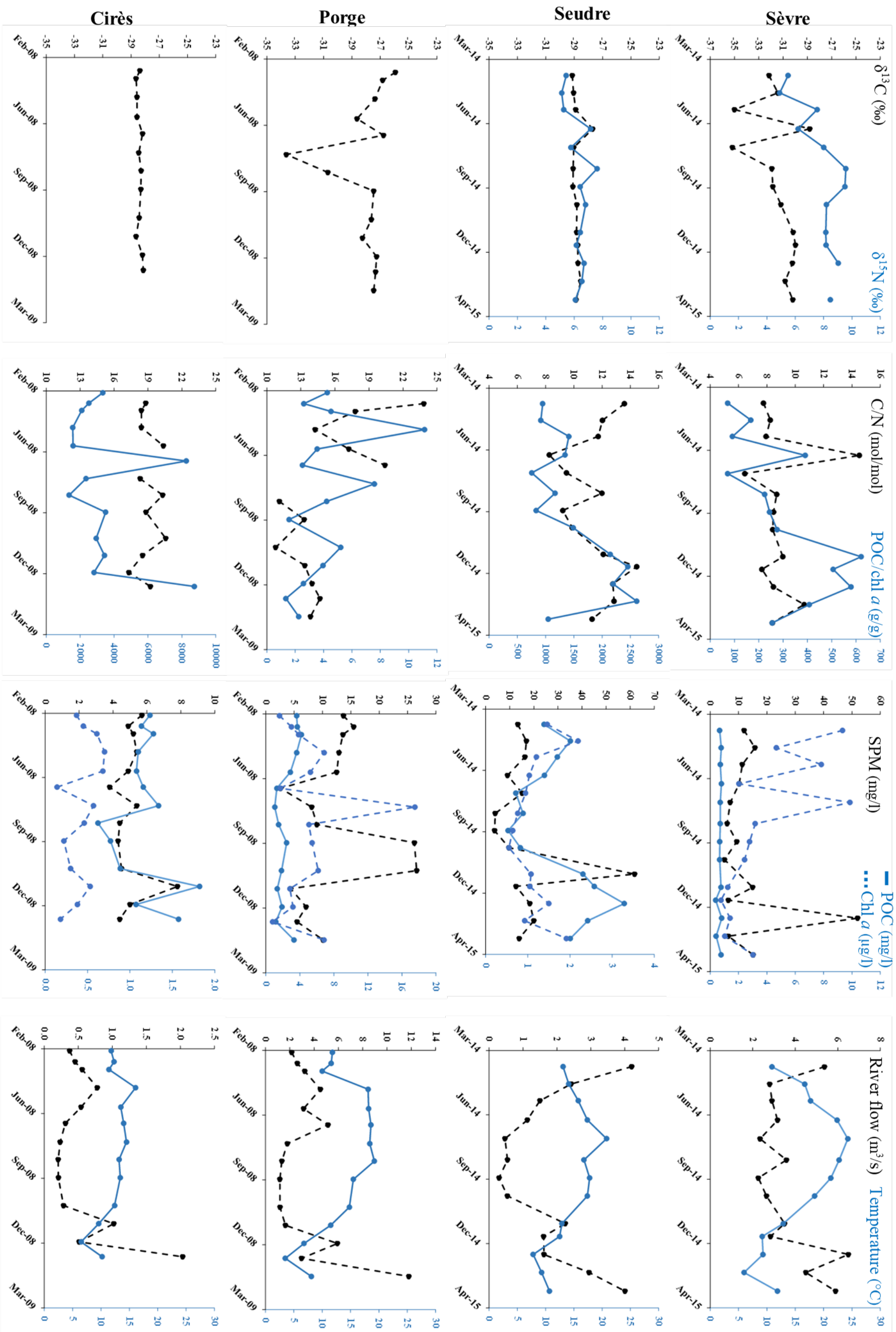

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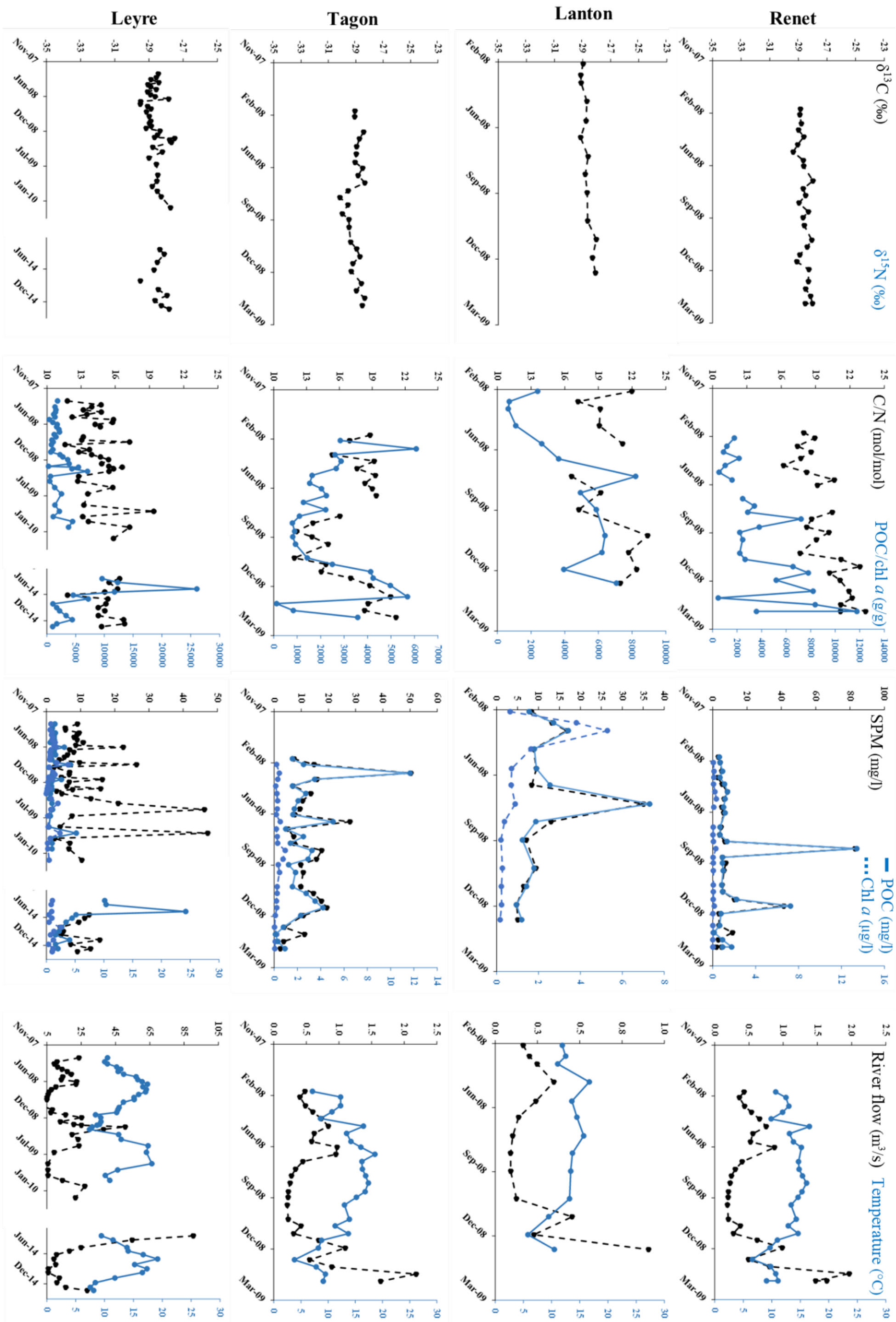

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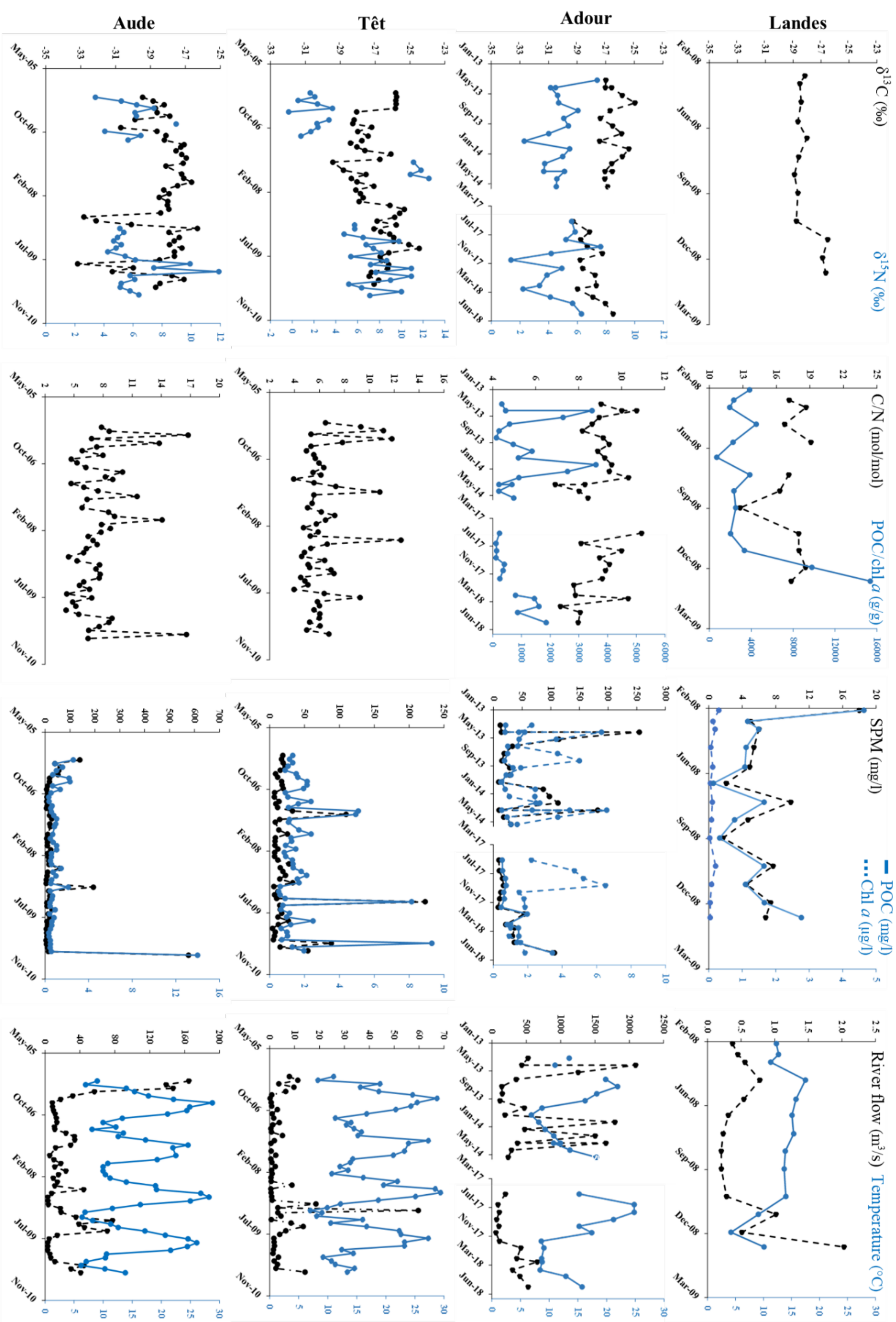

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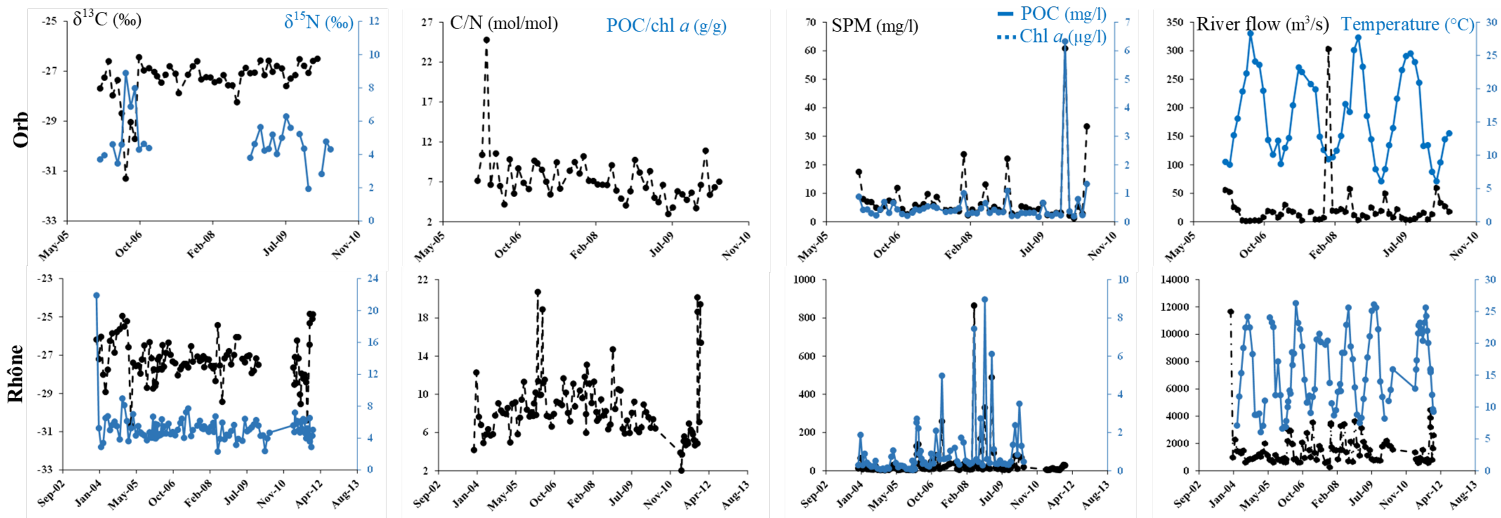

Figure A2 Temporal variations of matter characteristics for representative rivers along the studied periods for $\delta^{13}C$ (left axis; black dotted line) and $\delta^{15}N$ (right axis; blue line) (first column); C/N (left axis; black dotted line) and POC/chl a(right axis; blue line) ratios (second column); SPM(left axis; black dotted line), POC (right axis; blue line) and chl *a* (right axis; blue dotted line) concentrations (third column) and river flow (left axis; black dotted line) and temperature (right axis; blue line) (fourth column).

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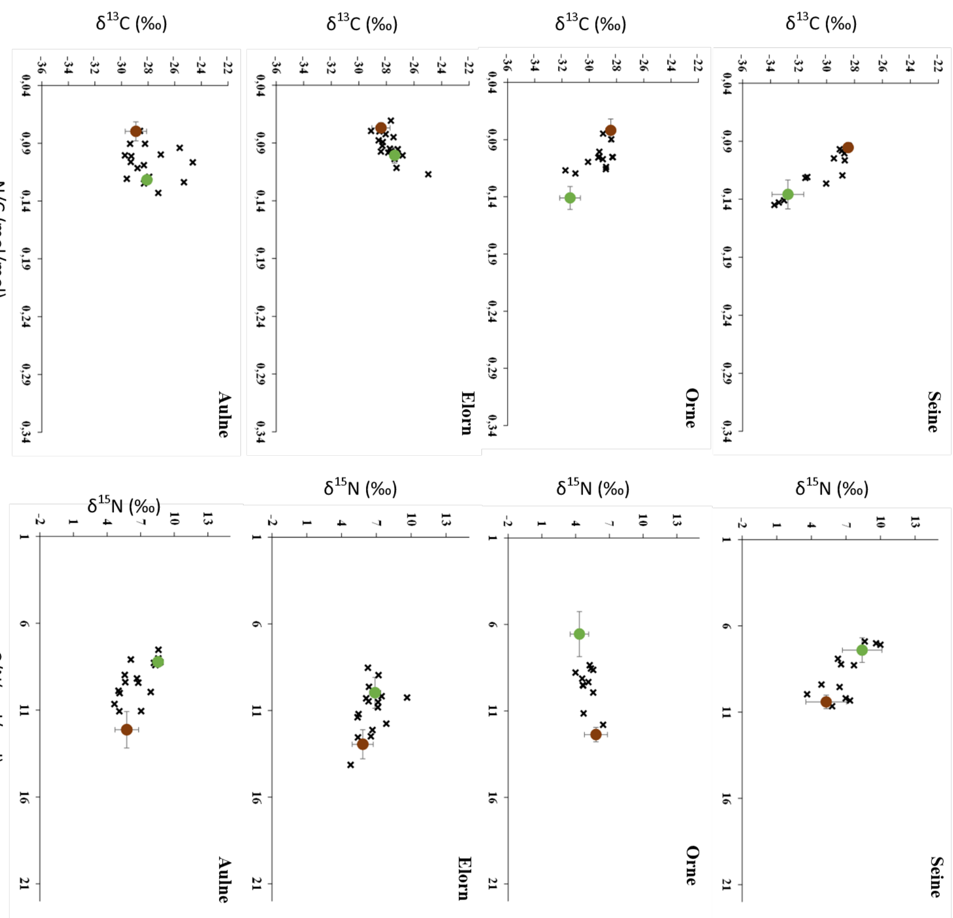

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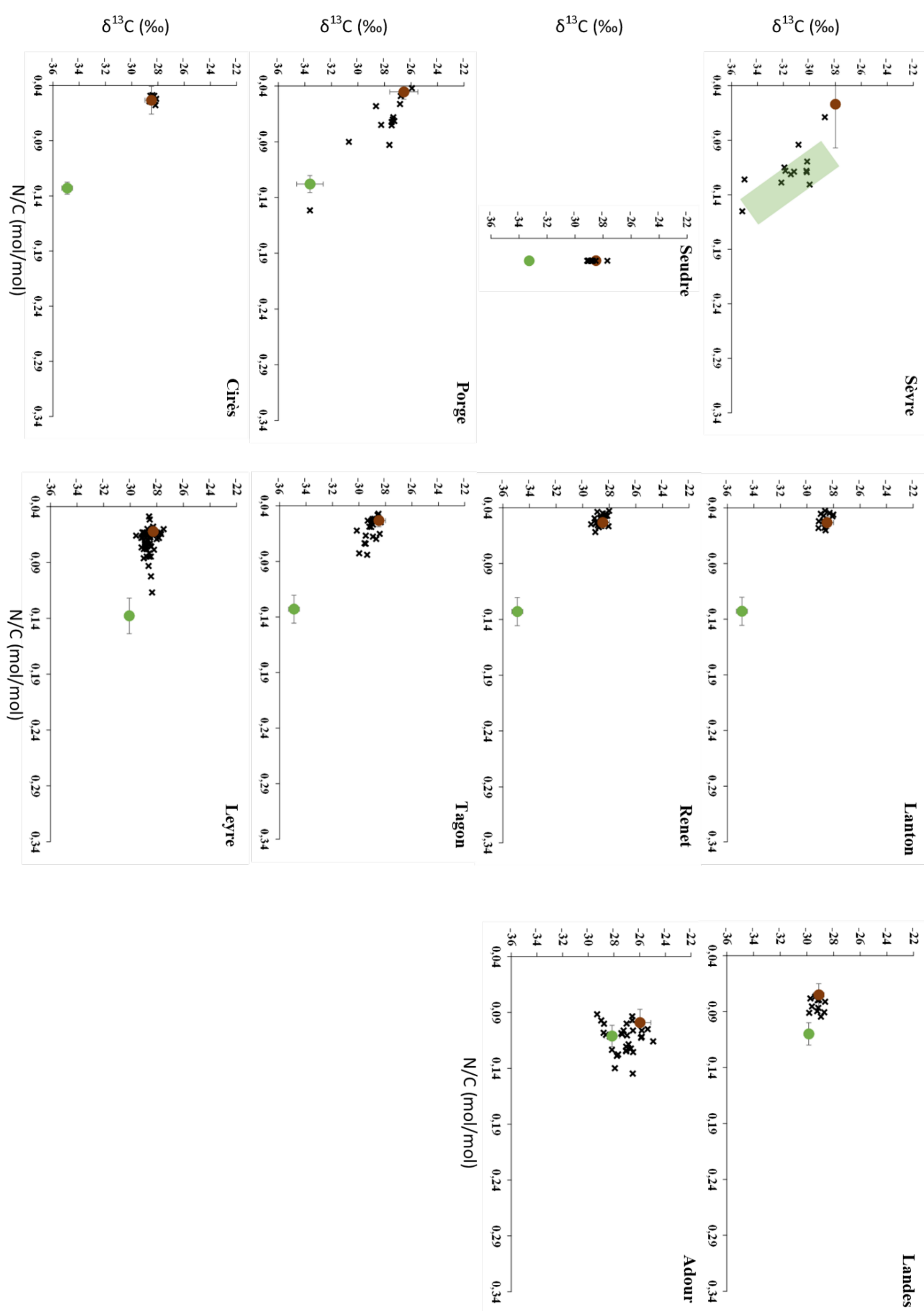

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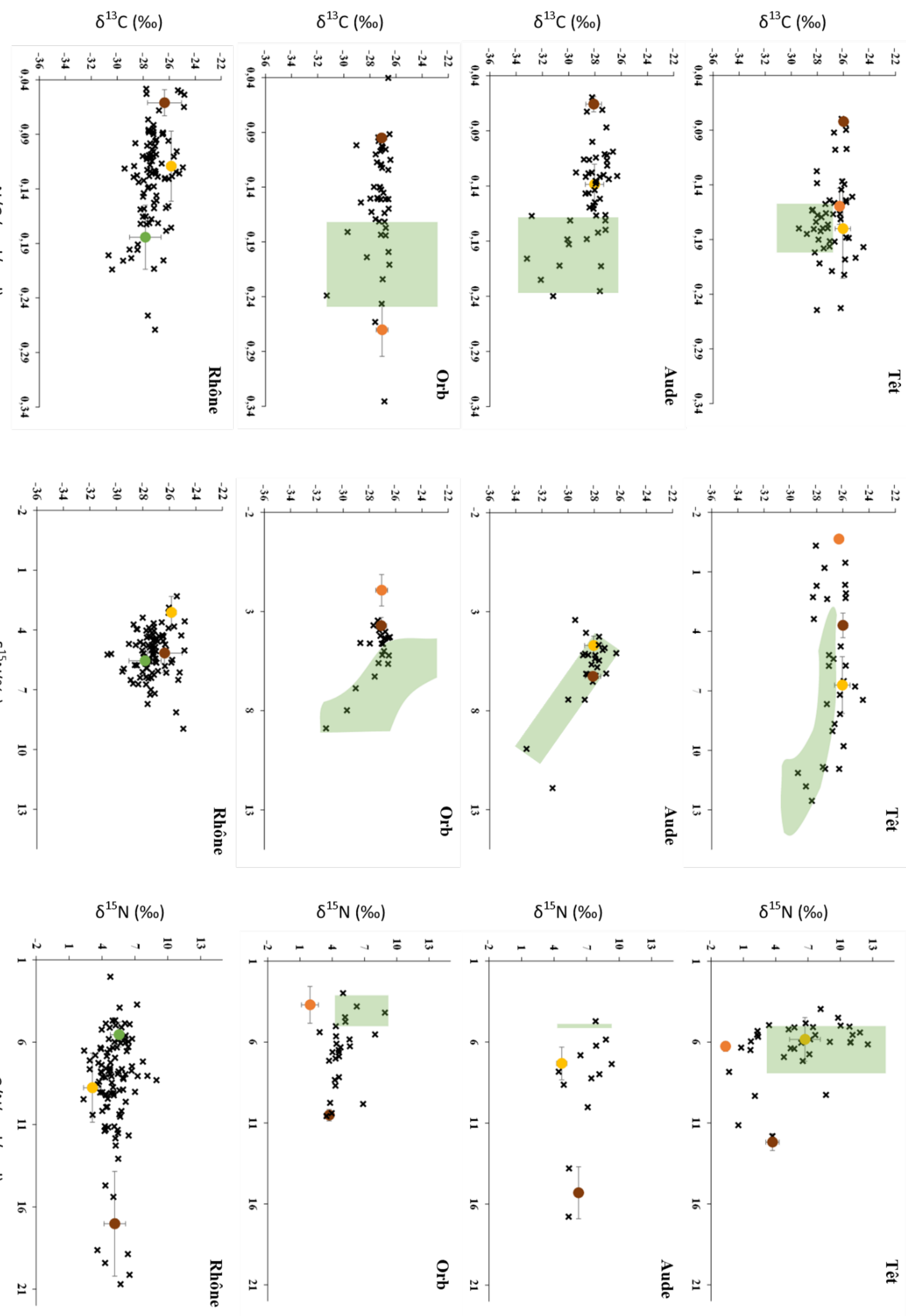

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Figure A3 $\delta^{13}C$, $\delta^{15}N$, N/C and/or C/N values of bulk POM (black crosses) and sources. The latter are presented as closed circles (average) and bars (standard deviation) when the signatures were constant over time and by colored area when at least one of the proxies was variable over time (see Table 2). This colored area corresponds to the dispersion of the values including their uncertainties.

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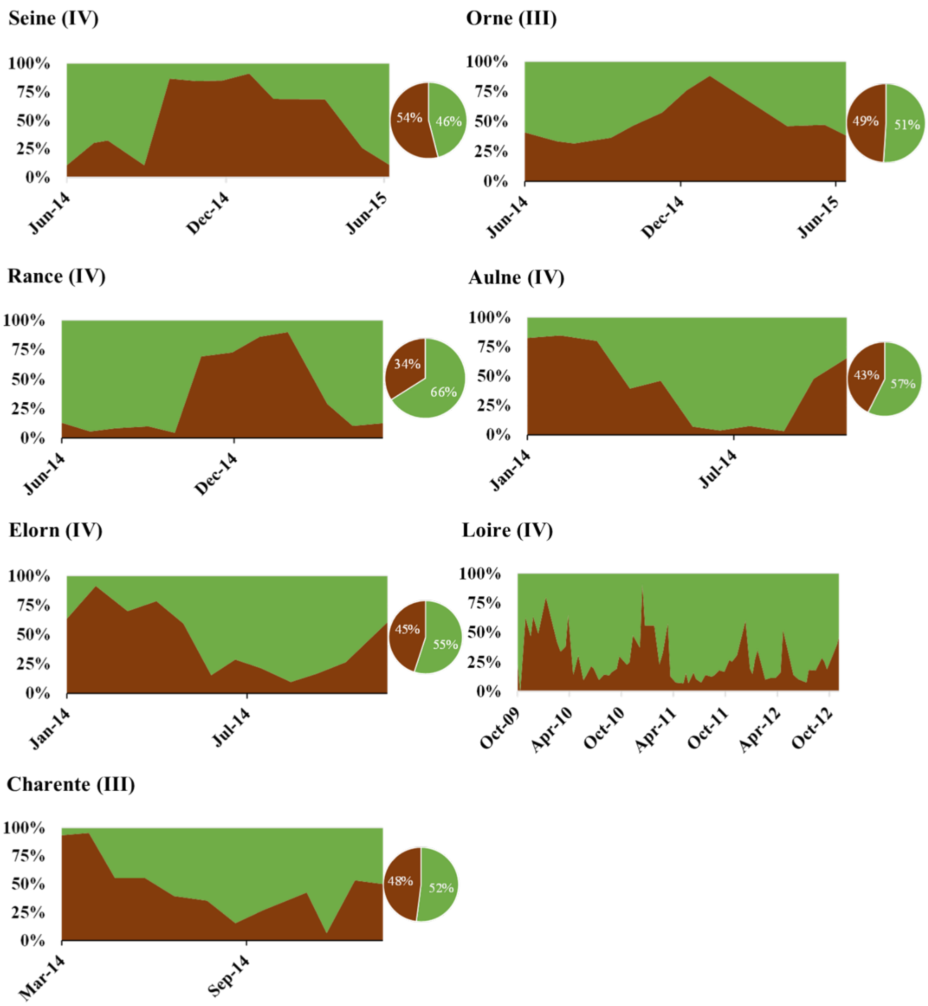

Figure A4 Temporal dynamic (rectangle graphs) and (inter-)annual mean (pie charts) of PN source proportions. Sources are phytoplankton (green) and labile terrestrial material (brown).

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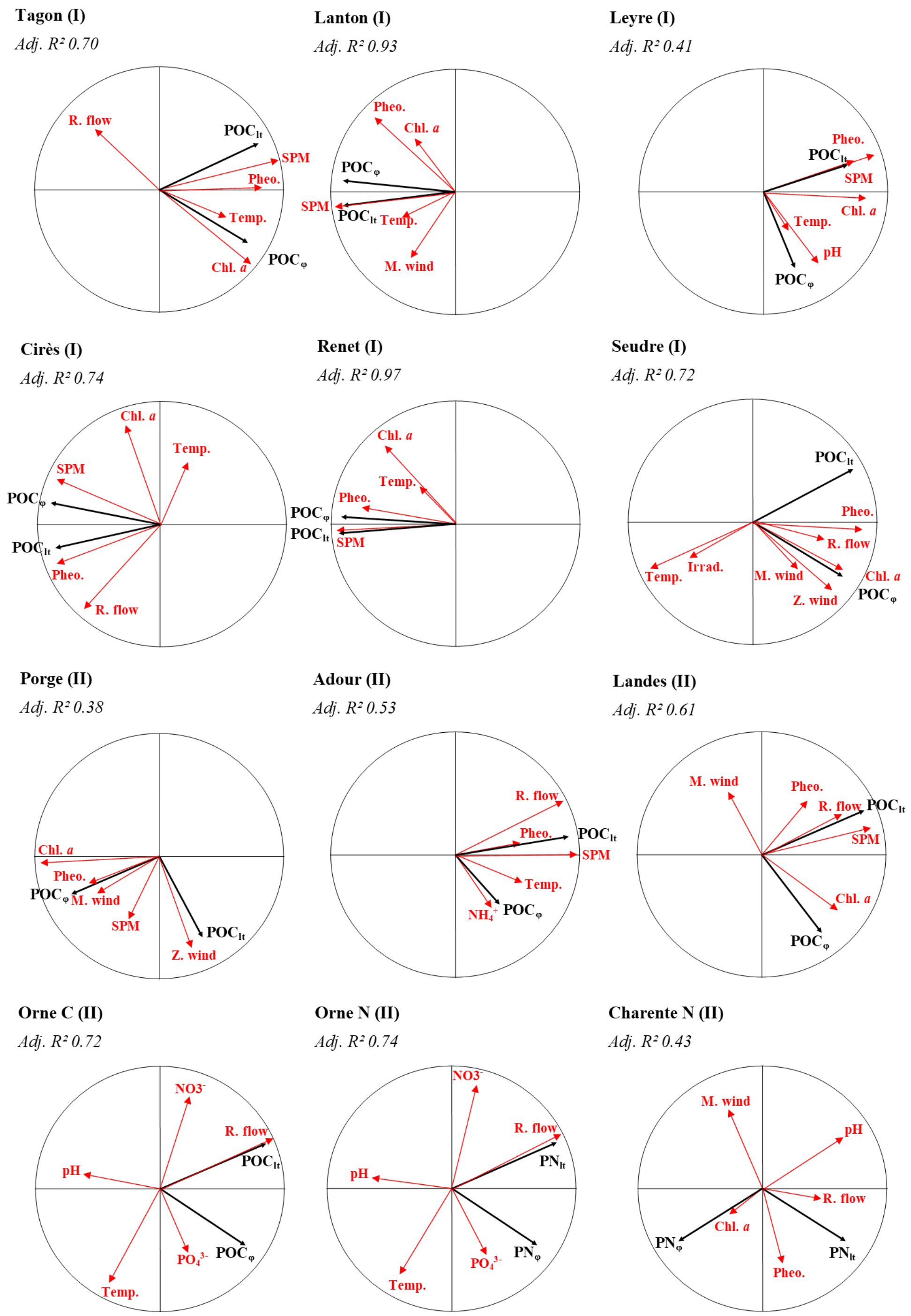

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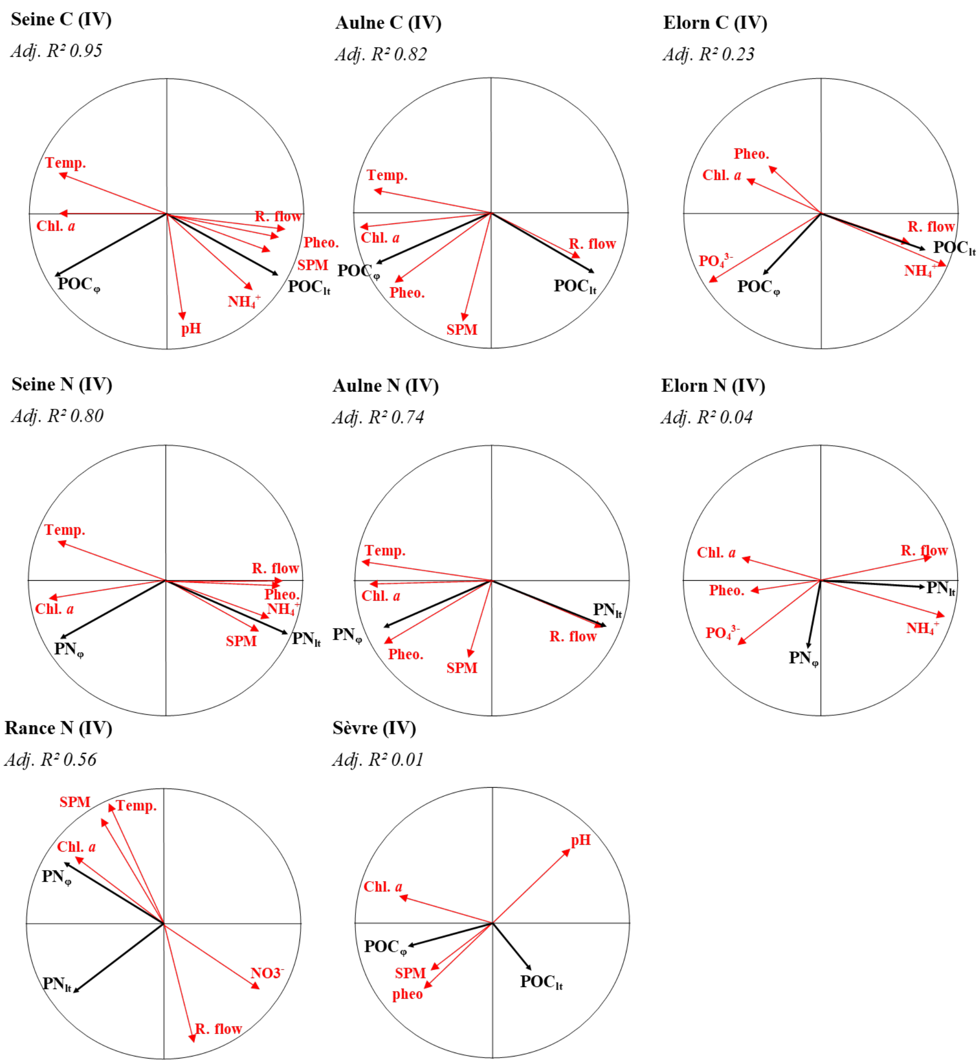

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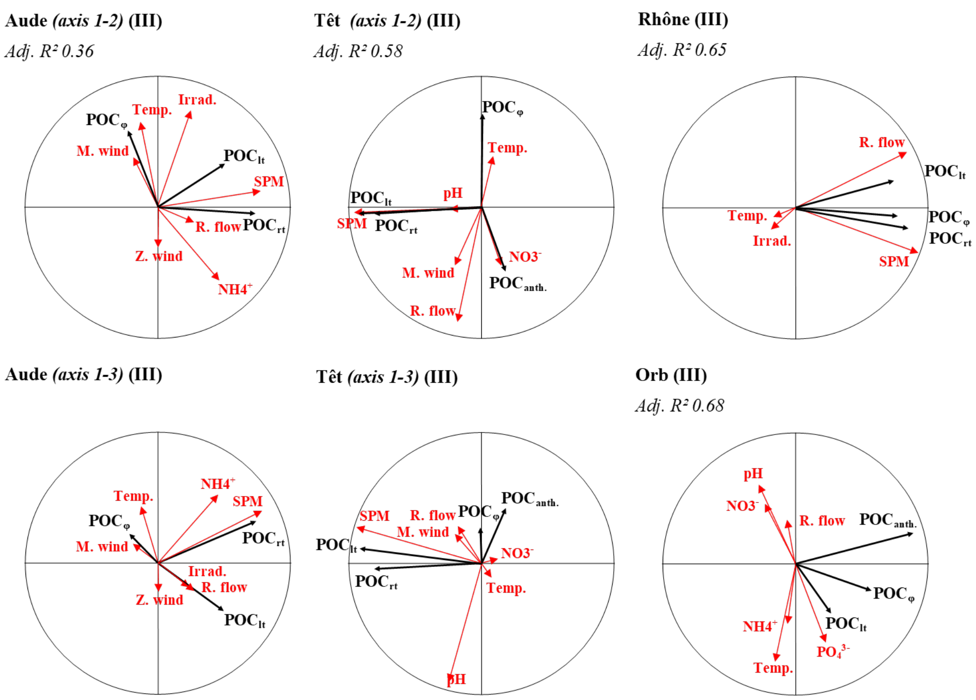

Figure A5 Redundancy analyses (correlation circles) of rivers standing for each type of river. Black arrows represent explained variables (concentration of POC or PN sources) and red arrows represent explaining variables (environmental variables). River types are recalled (Roman numerals). POC or PNlt = Labile terrestrial POC or PN; POCrt = Refractory terrestrial POC; POC or PNφ = Phytoplankton POC or PN; POCanth. = Anthropic POC; SPM = Suspended Particulate Matter; POC or PN= Particulate Organic Carbon or nitrogen; Chl. a = Chlorophyll a; Pheo. = Phaeopigments; R. flow = River flow; Temp. = Temperature; M. wind = Meridional wind; Z. wind = Zonal wind; Irrad. = Irradiance; NH_4^+ = Ammonium; NO_3^- = Nitrate; PO_4^{3-} = Phosphate; Adj. R^2 = adjusted R^2.

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Author contributions

FF: Formal analysis, Investigation, Visualization, Writing – original draft. CL: Formal analysis, Conceptualization, Supervision, Writing – original draft, Writing – review & editing. KC: Investigation. JD: Investigation, Visualization, Writing – review & editing. MG: Investigation. PK: Investigation. PP: Investigation, Visualization, Writing – review & editing.

NS: Conceptualization, Formal analysis, Investigation, Methodology, Supervision, Writing – original draft, Writing – review & editing.

Competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All POM and environmental data used in this article are stored in Figshare, accessible for the review process through this private link : https://figshare.com/s/a7101028e6ab5452c4db.

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