Regional trends in eutrophication across the Loire river basin during the 20th century based on multi-proxy paleolimnological reconstructions

Anthony Foucher, Olivier Evrard, Sylvain Huon, Florence Curie, Irène Lefèvre, Véronique Vaury, Olivier Cerdan, Rosalie Vandromme, Sébastien Salvador-Blanes

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Corresponding Author: Dr. Anthony Foucher,

Corresponding Author's Institution:

First Author: Anthony Foucher

Order of Authors: Anthony Foucher; Olivier Evrard; Sylvain Huon; Florence Curie; Irène Lefèvre; Véronique Vaury; Olivier Cerdan; Rosalie Vandromme; Sébastien Salvador-Blanes

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In this study, we used paleo-production proxies such as chlorophyll-a, organic matter properties (TOC and TN concentrations, δ13C and δ15N) measured in sediment cores dated with fallout 210Pbex and 137Cs activities for reconstructing changes in accumulation rates and sources of organic matter during the recent period of agricultural intensification (1920-2020). In order to record these changes at the regional scale, sediment cores were collected at the outlet of several headwater catchments (n=9), covering a wide range of land covers / land uses across the Loire River basin (117,000 km²), France.
The rates of sedimentary organic matter deposition in the studied water bodies accelerated from 1950 onwards (+48%). Between 1950 and 1970, the signature of sedimentary organic matter indicates a dominant contribution of soil-derived inputs. This period corresponds to major landscape modifications across the basin (land consolidation, stream re-design, implementation of tile drains) driving a general acceleration of erosion rates. Then, from 1960 onwards, chlorophyll-a and C/N proxies indicate an increase in primary production coupled with a decrease of terrigenous supply in agricultural catchments. These proxies were strongly correlated to the agricultural inputs during the 1955-1990 period (e.g., r=0.9 between chlorophyll-a content and N inputs), suggesting a progressive eutrophication of these reservoirs driven by increasing fertilizer use. During these 35 years, sedimentary organic matter deposition rates

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Anthony Foucher (1), Olivier Evrard (1), Sylvain Huon (2), Florence Curie (3), Irène Lefèvre (1), Véronique Vaury (2), Olivier Cerdan (4), Rosalie Vandromme (4), Sébastien Salvador-Blanes (3)

(1) Laboratoire des Sciences du Climat et de l'Environnement (LSCE/IPSL), UMR 8212 (CEA/CNRS/UVSQ), –Université Paris-Saclay, 91191 Gif-sur-Yvette Cedex, France
(2) Sorbonne Université, Institut d'Ecologie et des Sciences de l'Environnement de Paris (iEES), Case 237, 4 place Jussieu. 75252 Paris cedex 05, France
(3) Laboratoire GéoHydrosystèmes Continentaux (GéHCO), E.A 6293, Université F. Rabelais de Tours, Faculté des Sciences et Techniques, Parc de Grandmont, 37200, Tours, France
(4) Département Risques et Prévention, Bureau de Recherches Géologiques et Minières (BRGM), 3 avenue Claude Guillemin, 45060, Orléans, France

Abstract

Excessive inputs of sediment and acceleration of primary production have been observed worldwide in a large number of water bodies. Human-environment interactions were recognized as one of the main drivers of this evolution during the 20th century with the occurrence of major landscape changes and a greater use of agricultural inputs.

In this study, we used paleo-production proxies such as chlorophyll-a, organic matter properties (TOC and TN concentrations, $\delta^{13}C$ and $\delta^{15}N$) measured in sediment cores dated with fallout $^{210}Pb_{ex}$ and ^{137}Cs activities for reconstructing changes in accumulation rates and sources of organic matter during the recent period of agricultural intensification (1920-2020). In order to record these changes at the regional scale, sediment cores were collected at the outlet of several headwater catchments (n=9), covering a wide range of land covers / land uses across the Loire River basin (117,000 km²), France.

The rates of sedimentary organic matter deposition in the studied water bodies accelerated from 1950 onwards (+48%). Between 1950 and 1970, the signature of sedimentary organic matter indicates a dominant contribution of soil-derived inputs. This period corresponds to major landscape modifications across the basin (land consolidation, stream re-design, implementation of tile drains) driving a general acceleration of erosion rates. Then, from 1960 onwards, chlorophyll-a and C/N proxies indicate an increase in primary production coupled with a decrease of terrigenous supply in agricultural catchments. These proxies were strongly correlated to the agricultural inputs during the 1955-1990 period (e.g., r=0.9 between chlorophyll-a content and N inputs), suggesting a progressive eutrophication of these reservoirs driven by increasing fertilizer use. During these 35 years, sedimentary organic matter deposition rates increased on average by 30%. During the 1990s, despite a slight reduction in fertilizer use (-13%), the paleo-production proxies (e.g. chlorophyll-a) still indicate a positive trend suggesting the contribution of another driving factor such as climate warming or again nutrient release from soils and sediments.

In the absence of long term geochemical and sediment input monitoring, paleolimnological reconstructions provide a powerful tool to reconstruct past agricultural pressures in rural

environments. This study illustrates the impact of intensive farming on water body siltation driven by varying sources of organic material during the 20th century. In addition, these results suggest that eutrophication processes of these reservoirs with contrasting land uses started during the 1960-1970 period and are still ongoing nowadays.

Keywords: terrigenous organic matter, autochthonous production, agricultural inputs, agriculture intensification, soil erosion, Anthropocene

I. Introduction

Intensification of agricultural practices during the second half of the 20th century induced a significant acceleration of soil erosion and sediment delivery worldwide (Dearing & Jones, 2003; Cerdan *et al.*, 2010). This period of agriculture development is associated with a greater use of agricultural inputs including industrially produced fertilizers. Global fertilizer consumption was multiplied by 4.5 between 1960 and 2015 according to the FAO database (Tilman *et al.*, 2001; Lu & Tian, 2017). Both landscape management and the increase use of agricultural inputs have generated deleterious effects on terrestrial and aquatic ecosystems (e.g. Boardman & Poesen, 2006; Rowan *et al.*, 2012). Among these adverse consequences, the excessive delivery of sediment may contribute to the siltation of water bodies including dams, ponds, lakes or river systems (e.g. Gellis *et al.*, 2006; Downing *et al.*, 2008; Ahn *et al.*, 2010). Two main sources of material can contribute to this sediment accumulation: sediment originating from terrestrial sources (e.g. soil erosion, river channel erosion) including mineral and organic material supply or organic matter associated with excessive primary production induced by eutrophication (e.g. Meyers & Ishiwatari, 1995; Gudasz *et al.*, 2017). Causes and mechanisms of water body eutrophication were widely studied during the 1970s and 1980s in a large number of lakes in the Northern hemisphere (Glooschenko *et al.*, 1974; Hecky & Kilham, 1988). This research clearly outlined the key role of phosphorous (P) and nitrogen (N) point-based and diffuse source pollution in the bloom of algae in aquatic environments (Bennett *et al.*, 2001). Despite substantial management efforts implemented since this period to regulate agricultural N and P inputs and to improve wastewater treatment (EEC, 1991a; b), the excess of phytoplanctonic production remains problematic in coastal and continental waters (Le Moal *et al.*, 2019). According to the 2018 European water assessment status, at least 38% of the continental water bodies have agricultural diffuse source pollution in Europe (EEA, 2018).

In the absence of long term geochemical and algae production monitoring in river systems (Minaudo *et al.*, 2015; Chen *et al.*, 2016), trajectories of eutrophication and paleoproduction are less documented over the last century. Paleolimnological techniques based on the collection of sediment cores can provide a useful tool to reconstruct primary productivity over the last century (Brenner *et al.*, 1999; Anderson *et al.*, 2014). To this end, a large number of methods was developed in order to reconstruct changes in paleo-productivity in sediment cores (e.g. Meyers, 1994; Lu *et al.*, 2010), including the analysis of pigment contents in lake sediments (Waters *et al.*, 2005; Florian *et al.*, 2015). Chlorophyll-a and its degradation products are the most abundant pigments in lake sediments (Leavitt & Hodgson, 2001). They were widely analyzed for reconstructing histories of eutrophication, and assessing the respective impacts of human activities and climate change (Korosi & Smol, 2012; Stewart *et al.*, 2015). Chlorophyll-a concentration can be quantified through a wide range of chromatic techniques (Millie *et al.*, 1993; Hodgson *et al.*, 1997). In recent years, the potential of the rapid and non-destructive Visual Reflectance Spectroscopy has been demonstrated to detect chlorophyll-a and the associated pheopigments in sedimentary sequences (Wolfe *et al.*, 2006). In this way, a variety of indices were used to infer chlorophyll-a and its degradation products abundances including its relative absorbance depth at 660/670 nm (Rein & Sirocko, 2002), sediment reflectance near 675 nm (Wolfe *et al.*, 2006), the absorbance peak between 650 and 700 nm (Michelutti *et al.*, 2010) or again the Q7/4 ratio developed by Debret et al. (2011).

Stable C and N isotope signatures of sediment organic matter ($\delta^{13}C$ and $\delta^{15}N$) provide one of the most widely used methods to identify changes in sources of organic material. This methodology was applied to palaeoenvironmental reconstructions based on the analysis of lake sediments (e.g. Meyers, 1994; Huon *et al.*, 2018). The carbon isotopic composition of plants is variable and depends on the source of carbon assimilated. Terrestrial plant record $\delta^{13}C$ values range from -13 to -30‰ (C3 plants are associated with values of -23 to -30‰ whereas C4 plants correspond to values between -9 and -17‰ with an average value of -13‰) - (Meyers, 1994; Bowsher *et al.*, 2008). Freshwater aquatic plants and plankton have $\delta^{13}C$ values ranging between -25 and -30‰. Both terrestrial and aquatic organic matter may be distinguished through the comparison of their C/N ratio. Macrophyte residues have C/N ratios >20 but mineralization and aggregation in soils reduces C/N to *ca.* 10 (Meyers, 1994). In addition, $\delta^{15}N$ can provide information on biogeochemical processes including N consumption by organisms, varying sources of N, denitrification – nitrification and diagenetic processes (e.g. Jinglu *et al.*, 2007; Gälman *et al.*, 2009).

Although these proxies were widely used in sediment cores collected in estuarine, coastal areas or even in urban environments to investigate the relationship between nutrient inputs and a change in the water body trophic status (e.g. Voβ & Struck, 1997; Rabalais *et al.*, 2007), many fewer studies were conducted in small reservoirs located in continental environments. In addition, to the best of our knowledge, the study of freshwater reservoirs located in contrasted agricultural environments at the large basin scale (<100,000 km²) has never been conducted especially considering the second part of the 20th century.

The current research investigates the potential of sedimentary sequences collected at the outlet of contrasted rural catchments (with land cover dominated by forest, grassland or arable land) to reconstruct regional paleoproductivity trends. The objectives of this work are to determine the rates of organic matter deposition in sediments and to identify the sources of organic matter accumulated during the 20th century in these reservoirs, through the discrimination of the terrigenous (soil-derived) *vs.* autochthonous (biological) inputs. Finally, these results will be compared to available agricultural N input data and to current knowledge on soil erosion in these catchments.

II. Site and methods

1. Study sites

The Loire river basin (117,000 km², France) – (Fig. 1) is characterized by contrasted climate (annual rainfall varying between 600 and 1300 mm per year); landform (mean altitude = 300 m, 10% of the catchment >800 m); lithology (sedimentary; metamorphic and magmatic rocks) and land use conditions between its upper and lower parts (Fig.1). Characteristics of the studied sub-catchments were summarized in Table 1.

This large basin was impacted by major changes in agricultural practices during the second part of the 20th century. Some areas experienced an intensification of agricultural practices (mainly in the middle and lower catchment sections) - (Foucher *et al.*, 2014) whereas other parts were impacted by land abandonment following rural depopulation (mainly in upper parts of the catchment) - (Foucher *et al.*, 2019b) – Table 2. After 1950, the spreading of "NPK" fertilizers has significantly increased in France in particular in the Loire River basin (Poisvert *et al.*, 2017). In response to these changes, the Loire river basin – as most European basins – has been impacted by eutrophication processes. The first monitoring surveys focusing on primary production have demonstrated the pronounced eutrophic conditions of the Loire river in the early 1980s (Meybeck *et al.*, 1988; Etcheber *et al.*, 2007). A recent study showed that the continuous decline then stabilization of phosphate and nitrate concentrations in the river since 1990 led to the significant reduction of phytoplankton biomass across the whole river system (Minaudo *et al.*, 2015). Nevertheless, eutrophication still represents a crucial environmental problem in this basin nowadays. According to a recent report of the regional water agency, eutrophication remains one of the main causes of degradation of the ecological status of water bodies (lakes, ponds, dams, etc.) with 29% of those in medium ecological status, 18% in low ecological status and even 26% in bad ecological status (AELB, 2013).

Nine reservoirs (lakes and ponds, with a surface ranging between 1.2 and 57 ha) located at the outlet of rural catchments (<100km²) were selected in various environments across the Loire river basin to reconstruct trends in rates of sedimentary organic material deposition and to identify the sources of sediment (Fig. 1). These reservoirs were selected among the 14,000 natural and artificial water bodies of the Loire basin because their catchment histories are well known. Furthermore, to the best of our knowledge, these reservoirs were never dredged or drained during prolonged periods. These water bodies are mainly artificial (n=8 artificial and one natural (Tazenat lake)) and they are connected by ephemeral river networks to their drainage area during heavy rainfall. These sites were selected in order to be representative of the diversity of landscape, climate, topography and agricultural practices found across the Loire basin. Although they are unevenly distributed in space across the basin, they cover all the characteristics of the agricultural landscapes found in this region. Among these catchments, four are mainly covered with grassland, three with arable land and two with forests.

The characteristics of these catchments are summarized in Table 2.

2. Materials and methods

Fieldwork was conducted between January 2017 and June 2018. Sediment cores (n=9) were collected in the nine water bodies using an Uwitec gravity corer (Uwitec®, Mondsee, Austria) equipped with a 90 mm PVC liner and a floating platform available at the Tours University (GeHCo laboratory, France). In each artificial reservoir, the sediment core was collected in the dam vicinity (≈50 to 100m from the dam) in the zone where the sedimentation rates are the highest. In the natural reservoir of Tazenat, the sediment core was retrieved in the center of the water body. Given the relatively small size of these reservoirs (<52 ha), it is assumed that the sediment properties recorded at these sampling sites are representative of those found across the entire water bodies with the exception of variations for the sedimentation rates.

Sampling locations and bathymetric data were recorded using a Garmin® Echomaps depth sounder (Garmin, Lenexa, USA).

2.1. Chronology

Sediment dating of the nine cores (selected to be representative of the entire water bodies) were established using Caesium-137 (^{137}Cs) and excess Lead-210 ($^{210}Pb_{ex}$) activities measured in 130 samples of dried sediment material (*ca* 10g). These samples were regularly collected along the sediment cores with on average one sample taken every 6 cm. Gamma spectrometry measurements were obtained using coaxial N- and P- type HPGe detectors (Canberra/Ortec®) available at the Laboratoire des Sciences du Climat et de l'Environnement (Gif-sur-Yvette, France). The ^{210}Pb activities were determined at 46.5 keV. $^{210}Pb_{ex}$ was calculated by subtracting the supported activity from the total ^{210}Pb activity (measured at 46.5 keV) using two Radium-226 daughters, Lead-214 (average count at 295.2 and 351.9 keV) and Bismuth-214 (609.3 keV). All measurements were corrected for background level determined every two months as well as for detector and geometry efficiencies. Activities were also decay-corrected to the sampling date (Evrard *et al.*, 2016).

Age of the sediment sequence layers was determined using the Constant Rate of Supply model (CRS), (Appleby & Oldfield, 1978). This model assumes a constant rate of $^{210}Pb_{ex}$ supply from atmospheric fallout, although sediment accumulation is allowed to vary throughout time. For improving the $^{210}Pb_{ex}$ age model of some cores, the corrected CRS model described in Appleby (2001) was used. The $^{210}Pb_{ex}$ age model validation was carried out through the identification of ^{137}Cs peaks in the sedimentary sequences. This artificial radionuclide may originate from two sources in Western Europe: the Chernobyl accident (1986) and the thermonuclear weapons testing (maximal emissions in 1963). Fukushima fallout was shown to be negligible in France (Evrard *et al.*, 2012). To distinguish between both potential ^{137}Cs sources, Americium-241 (^{241}Am), a daughter product of plutonium-241, was used to identify the ^{137}Cs peak attributed to the maximum nuclear bomb fallout of 1963 (e.g Cambray et al., 1989). Information related to sediment core dating was summarized in Table 3.

2.2. Laboratory analyses

Measurements of Visible Reflectance Spectroscopy (VRS) were obtained using a portable spectrophotometer (Konica® Minolta 700-D) equipped with a 3 mm target radius. Spectral reflectance was measured between 400 and 700 nm, with a 10 nm resolution. Before each set of measurements, the device was calibrated using a white and black calibration box.–Measurements were continuously recorded on the fresh sediment surface with a 1-cm resolution, in each core.

The absorbance peak between 650 and 700 nm was extracted for a sequence of samples selected in the sedimentary sequences to cover 5-year periods on average as a spectral index to measure the summed concentration of all compounds associated with both primary and degraded chlorophyll-a (chlorophyll-a + all chlorophyll-a isomers + pheophytin-a + pheophorbide-a) - (Michelutti & Smol, 2016). The area under the absorbance peak from 650 to 700 nm was calculated following the procedure described in Das *et al* (2005). These values provide a relative information on chlorophyll-a occurrence index derived from the true area calculation. In order to reduce the noise of the colorimetric time series, a LOESS smoothing model was applied using the free software PAST 3 (Hammer *et al.*, 2001).

The occurrence of carbonate minerals was determined for 95 samples selected on the 9 master cores (on average one sample every 5 years) with a Bernard calcimeter (University of Tours, France) following the method described in NF ISO 10693 (1995). When detected, carbonates were systematically removed from the sample aliquots before performing analyses to determine the total organic carbon concentration (TOC) and stable C isotopes ratios of organic matter and clay-bound organic matter. To reduce possible leaching effects on sedimentary organic matter during carbonate removal, sediments were carefully treated with a 1N HCL solution during 96 hours under constant agitation and pH control in order not to drop below 2.5. Powder X-ray diffraction controls were conducted to ensure the full dissolution of all carbonate minerals in the sediment residue (calcite, dolomite, ankerite, ...). All the samples were rinsed six times in deionized water to remove dissolved salts. The solid residues were recovered by high velocity centrifugation (2500 rounds.min^{-1}) for 15 minutes each time (Huon *et al.*, 2002).

On these decarbonized sample aliquots, EA-IRMS analyses were conducted on dry sediment for elemental concentration (TOC and total nitrogen concentration TN) and stable C and N isotopes ($\delta^{13}C$, $\delta^{15}N$) measurements. These measurements were performed with a continuous flow Elementar® VarioPyro cube elemental analyzer (EA) coupled to a Micromass® Isoprime Isotope Ratios mass Spectrometer (IRMS) at the Institute of Ecology and Environmental Science of Paris. Oxygen for combustion was injected during 70 s (30 mL min^{-1}) and temperatures were set at 850 °C and 1120 °C for the reduction and combustion furnaces, respectively (Agnihotri *et al.*, 2014). Analytical precision and repeatability were controlled with tyrosine samples calibrated against international standards (Coplen *et al.*, 1983). In the current research, the mean uncertainties were 0.2 ‰ for TN, 0.18 ‰ for TOC, 0.1 ‰ for $\delta^{13}C$ and 0.2 ‰ for $\delta^{15}N$.

2.3. Mass accumulation rate of organic material

Organic matter Mass Accumulation Rates (MARorg, expressed in gC cm^{-2} yr^{-1}) were estimated for each individual core using the Sediment Accumulation Rate (SAR, cm yr^{-1}, estimated with the $^{210}Pb_{ex}$ decay), the Dry Bulk Density (DBD, expressed in g cm^{-3} and calculated by measuring the amount of dry sediment in a known volume) and the total organic carbon concentration (TOC, expressed in gC g^{-1}) following eq. 1. MARorg corresponds to the amount of organic material deposited at each individual coring site. This sediment may originate from terrestrial inputs (allochthonous inputs) or may be directly produced in the water body (autochthonous production).

$$MARorg\ [g\ cm^{-2}\ yr^{-1}] = DBD\ [g\ cm^{-3}] \times SAR\ [cm\ yr^{-1}] \times TOC\ [gC\ g^{-1}] \quad \text{(eq. 1)}$$

2.4. Agricultural inputs

Data from the CASSIS_N model (www.geosciences.univ-tours.fr/cassis) - (Poisvert *et al.*, 2017) was extracted for each individual catchment and for the entire Loire river basin. This model was used for estimating the mineral and organic nitrogen (N) consumption expressed in $kg.ha^{-1}$. This model based on data from agricultural census is available between 1955 and 2015 with an annual resolution.

2.5. Statistical analyses

The Mann-Kendall non-parametric test (MK-test) was used for detecting monotonic trends in temporal series (Warren & Gilbert, 1988). In this study, the temporal series correspond to the evolution of production proxies ($\delta^{13}C$, $\delta^{15}N$, TN, TOC, chlorophyll-a), MARorg, MARmin as well as agricultural inputs throughout time. This test was applied to confirm the occurrence of monotonic upward or downward trends of a given variable throughout time (P-value < 0.05). Trends can be positive, negative or non-null.

The non-parametric Buishand test (BU-test) was used for detecting the occurrence of changes in temporal series (Buishand, 1982). Buishand test with a P-value < 0.05 indicated a heterogeneous temporal trend between two periods.

In addition, the correlation coefficient (denoted r) was used to quantify the direction (positive, negative) and strength of the linear association between two variables.

3. Results

3.1. Chronology

According to the dating models, the deepest sediment layers in the cores were deposited before 1925 (n=8) except for a single core where it is assumed to have deposited after 1950 (Table 3). The age controls provided by the detection of artificial radionuclides (^{137}Cs and ^{241}Am) were identified in four reservoirs for the Chernobyl fallout and in eight sequences for the 1963 fallout (Fig 4, 5 and 6). Errors between continuous $^{210}Pb_{ex}$ age models and those obtained with the radiocesium were in average of 2 years for 1986 and 3 years for 1963. Chronology of two cores, respectively those of the Prugnolas pond and Malaguet lake (Fig. 1) was detailed in Foucher *et al.* (2019b; a). Chronology of the nine cores is detailed in Table 3.

3.2. Trends in paleo-production proxies

Organic material production has significantly changed in seven of the nine study sites with a statistical increase of TOC concentrations in five of the reservoirs. For the two catchments dominated by forests, TOC contents varied between 94 and 180 gC kg^{-1} (average value of 130 ± 24 gC kg^{-1}) – (Fig. 2). A non-significant trend in TOC content was recorded at both forested sites (P >0.05 MK-Test) – (Table 4). TOC content in catchments mainly occupied by grassland ranged between 18 and 160 gC kg^{-1} (average value of 50 ± 29 gC kg^{-1}) – (Fig. 3). Content in organic material increased by

0.04, 1.6, 2.6 and 7.8 % after 1950 (for Loroux, Goule, Beaurepaire and Tazenat reservoirs, respectively). The Loroux pond did not record any statistical change in TOC content. Nevertheless, a peak of organic material was identified in 1965 (TOC = 75 gC kg^{-1}) – (Fig. 3). For the Malaguet lake, this peak was identified in 1956 (TOC = 159 gC kg^{-1}) – (Fig. 2). During the same period, Tazenat lake recorded an acceleration of organic material accumulation, with TOC contents increasing from 2.6 to 7.6 % (between 1950 and 1958). TOC concentrations measured in the three study sites dominated by arable land ranged between 28 and 157 gC kg^{-1} (average value of 65 ± 28 gC kg^{-1}) – (Fig. 4). Concentration in organic material decreased by 0.1 and 1.1% (for Brosse and Passavant ponds, respectively) although it increased by 1.3 % for the Boisvinet pond during the last century. Brosse and Passavant ponds recorded an acceleration of organic material accumulation in the middle of the 20^{th} century (respectively between 1952 and 1960 (TOC = 157 gC kg^{-1}) and between 1955 and 1966 (TOC = 95 gC kg^{-1}) – (Fig. 4).

During the 20^{th} century, $\delta^{13}C$ results showed a significant positive trend in six of the studied reservoirs with a switch around 1973 ± 11 yr in grassland environments, in 1969 in catchments dominated by forest and in 1984 ± 1 yr in areas mainly occupied by arable land (Table 4). For the three remaining water bodies (Brosse, Boisvinet and Prugnolas pond), no statistical trend was observed (Table 4). In forested catchments, $\delta^{13}C$ ranged between -27.4 ‰ and -29 ‰ (average value of -28 ± 0.4 ‰) – (Fig. 2). For the Malaguet lake, the $\delta^{13}C$ decreased by 0.3 ‰ during the covered period while it decreased by 0.6 ‰ during the last century in the Prugnolas pond. For the pond located at the outlet of catchments dominated by grassland, the $\delta^{13}C$ signature of organic matter ranged between -26.7 ‰ and -30.5 ‰ (average value of -28.6 ± 0.95 ‰) – (Fig. 3). For these four catchments, $\delta^{13}C$ values decreased by 0.5, 0.6, 1.7 ‰ and increased by 0.54 ‰ during the 20^{th} century (for the Beaurepaire, Goule, Tazenat and Loroux ponds, respectively). The $\delta^{13}C$ of organic matter measured in sediment cores collected in reservoirs draining catchments under arable land ranged between -26.7 ‰ and -32.3 ‰ (average value of -29.3 ± 1.4 ‰) – (Fig. 4). Values prior to 1950 were in average of -28.6 ± 1.7 ‰ compared to -29.5 ± 1.1 ‰ afterwards. During this period, $\delta^{13}C$ values decreased by 1.6 ‰ and 0.32 ‰ (for Passavant and Boisvinet ponds, respectively) and increased by 0.2 ‰ in Brosse Pond.

The $\delta^{15}N$ signature of organic matter displayed a significant positive trend in three reservoirs (Beaurepaire, Passavant and Boisvinet) and a negative trend in two other water bodies (Loroux and Prugnolas ponds) – (Table 4). Regarding the observed positive trend, the change in trajectory was recorded to occur around 1977 ± 11 yr while it started in 1976 ± 26 yr for negative trends. For the four remaining sites located under various land covers, no statistical trend was recorded (Table 4). For the forested catchments, $\delta^{15}N$ decreased by 0.2 ‰ and 1.3 ‰ (for Malaguet and Prugnolas reservoirs, respectively) during the documented periods (Fig. 2). Under grassland environments, these values ranged between 4.1 ‰ and 8.8 ‰ (average 7 ± 1.4‰). $\delta^{15}N$ increased by 0.3‰ in the Beaurepaire pond and decreased by 0.4, 0.6 and 2.2 ‰ during the last century (for Goule, Loroux and Tazenat study sites, respectively) – (Fig. 3). In catchments dominated by arable land, $\delta^{15}N$ ranged between 4.4 ‰ and 8.1 ‰ (± 5.7 ‰). When comparing values recorded prior to and after 1950, $\delta^{15}N$ increased by 0.5, 1 and 1.1 ‰ (for Brosse, Boisvinet and Passavant ponds, respectively) – (Fig. 4).

C/N ratios showed a significant negative trend in only two ponds (Loroux and Goule ponds) with a switch in this trend occurring around 1969 ± 6 yr. For these two reservoirs, C/N ratio increased from 7.3 to 9.5 for the Goule pond and from 8.6 ± 0.2 to 8.9 ± 0.6 for the Loroux pond, in 1950 and 2010, respectively (Fig. 3)

Statistical positive trends in chlorophyll-a were recorded in seven reservoirs. Only the Prugnolas pond and the Tazenat lake did not show any statistical trend (Table 4). In the forested catchment, this increase reached around 160 ± 205 % (Fig. 2). In catchments dominated by grassland, chlorophyll-a values increased by 136 ± 87 % after 1950 (Fig. 3). During this period, an increase of 190 ± 160 % was recorded in arable land environments (Fig. 4). Changes in these trends were recorded around 1996 ± 5 yr 1963 ± 7 yr and 1990 – for catchments dominated by arable land, grassland, and forest, respectively.

3.3. Mass accumulation rate of organic material

Accumulation rate of sedimentary organic material (originating from soil erosion and autochthonous production) has significantly changed during the last century. In the two catchments occupied by forest, negative trends were recorded (decrease of 160 ± 100% – Table 4). In these catchments, the deposition rates started to decrease around 1963 ± 23 yr (Fig. 5). A significant positive trend in organic production was recorded in the four catchments occupied by grassland (MK test P <0.05) – (Table 4). In this context, organic matter deposition rate increased on average by 58 ± 23 % between 1950 and 2015 (Fig. 5). In catchments dominated by arable land, a positive trend was only recorded in one catchment (Boisvinet catchment) with an acceleration of organic accumulation around 1970. For the five catchments recording a positive trend, the average rate of deposition raised from 67 ± 35 gC m^{-2} yr^{-1} before 1950 to 134 ± 66 gC m^{-2} yr^{-1} after 1950 (Fig. 5). In the two reservoirs where no statistical trend was observed (MK test P < 0.05) - (Brosse and Passavant reservoirs), a significant increase of productivity was recorded between 1940 and 1975 (Fig. 5). On average, rates of organic deposits reached 260 ± 44 gC m^{-2} $year^{-1}$ before 1950, 350 ± 302 gC m^{-2} $year^{-1}$ between 1950 and 1975 and 318 ± 126 gC m^{-2} $year^{-1}$ after 1975.

3.4. Agricultural inputs

The analysis of N fertilizer inputs (mineral + organic) of the nine selected catchments shows the occurrence of three main trends. In the six catchments occupied by arable land and grassland, a significant increase in N fertilizer use was observed during the last century (MK test P < 0.05) - (Table 4) In these sites, a major acceleration occurred around 1966 ± 5 yr (BU test) – (Fig. 6). On average, this consumption started to stabilize or to decrease in 1994 ± 5 yr. For these catchments, consumption of N fertilizers increased on average by 60 ± 10% for the 1955-2015 period. No statistical trend (MK test P > 0.05) was observed for the Boisvinet catchment (site 5, Fig. 1) located in lowland environments dominated by arable land (Table 2).

Finally, the two catchments currently occupied by forest displayed a negative or the absence of any significant statistical trend in N fertilizer inputs (for the Malaguet and the Prugnolas catchment, respectively) – (Table 4). For the Malaguet site, a significant decrease in consumption was recorded around 1975. The use of N fertilizer inputs decreased by 20 % at this site (Fig. 6).

4. Discussion

Local records

The non-linear decrease and the independent variation of paleo-production proxies through time (chlorophyll-a, sedimentary bulk organic matter $\delta^{13}C$ and $\delta^{15}N$ and C/N concentration) does not suggest the post-depositional degradation of organic matter as no typical increasing logarithmic trend of TOC and TN concentrations was observed in the upper part of the sediment cores (Fig. 2, 3 and 4) - (Emerson *et al.*, 1985; Arndt *et al.*, 2013). Variation in individual proxies can therefore be attributed to a change in organic matter sources.

Results obtained on the nine sedimentary sequences collected at the outlet of contrasted catchments showed variable contributions of terrestrial versus autochthonous organic matter during the 20th century. These changes in organic matter sources were attributed to anthropogenic pressures observed in the landscape, with the intensification of anthropogenic activities and a greater use of agricultural inputs (e.g. Schindler Wildhaber *et al.*, 2012).

In the two forested catchments, the period prior to 1960 was characterized by the highest C/N ratios recorded in this study (ranging between 17 and 24), suggesting the dominant delivery of vascular debris (C/N >20 from vascular plants (Meyers, 1994)). These results were in agreement with our historical knowledge on the processes occurring in these catchments. During the 20th century, both catchments were affected by land abandonment, evolving from an open landscape, mostly occupied by grassland, to forested catchments. Between 1950 and 1960, major afforestation works were conducted in the Malaguet catchment inducing a significant acceleration of soil erosion (Foucher *et al.*, 2019b). The forest regrew spontaneously in the Prugnolas catchment and, as a consequence, soil erosion decreased progressively during the 20th century. The increase of values recorded by terrigenous organic matter proxies (C/N, TOC concentration) during the 1950-1960 period was recorded during this period of afforestation, soil disturbance and soil erosion. After this period, organic sediment sources have drastically changed as reflected by an increase of TOC contents in sediment (from 130 to 170 gC kg^{-1} and from 110 to 150 gC kg^{-1}) as well as a decrease in the C/N ratios (from 24 to 13 and from 16 to 11, for Prugnolas and Malaguet reservoirs, respectively) – (Fig. 2). In contrast, during this period, chlorophyll-a increased (450% and 160% for Prugnolas and Malaguet reservoirs, respectively). The strong negative relationship observed between chlorophyll-a and $\delta^{13}C$ (r = 0.99 and 0.87 for Prugnolas and Malaguet reservoirs, respectively) suggests a greater contribution of autochthonous production during the second half of the 20^{th} century. During this period, agricultural inputs remained constant or even decreased (Fig. 6), and they were not correlated to paleo production proxies (e.g. correlation between chlorophyll-a vs N inputs r = 0.02 and 0.5 for Prugnolas and Malaguet lakes). In the Prugnolas catchment, the increase of ^{137}Cs activities recorded in sediment deposited after 1999 was attributed to a greater contribution of surface soil erosion during a landscape management period following the major 1999 windstorm (Foucher *et al.*, 2019a). During this period both TN concentration and $\delta^{15}N$ increased as well as chlorophyll-a values (r = 0.98 and 0.99, respectively) – (Fig. 2). Acceleration of autochthonous production during the last 25 years can be therefore attributed to a release of soil nutrients.

In grassland areas (drained by the Beaurepaire, Tazenat and Loroux-Bottereau reservoirs), changes in sedimentary matter signatures were also recorded during the 20^{th} century. Between 1950 and 1970, a general increase in TOC contents (on average 120 ± 110 %) associated with higher C/N organic ratios (average value of 9.5 ± 1), an increase of MARorg rate (140 ± 70%) and changes in $\delta^{13}C$ and $\delta^{15}N$ proxies were observed (Fig. 3). A similar observation was made in catchments dominated by arable land (Passavant and Brosse basins). During this same period, TOC contents increased on average by 63 ± 1 % and were associated with an acceleration of MARorg deposition (84 ± 40 %) and high C/N (11.5 ± 0.5). In addition, this period corresponds to an increase of ^{137}Cs activity suggesting a mobilization of material originating from surface soil sources (Olley *et al.*, 2013) for le Loroux, Beaurepaire, Tazenat and Passavant catchments (Fig. 3 and 4).

In both contexts of arable land and grassland, this post Second Word War (WWII) period corresponds to a phase of intensification of agricultural practices across the Loire river basin, with the implementation of major landscape modifications (e.g. land consolidation corresponding to the reorganization and the increase of plot size, stream redesign, tile drain creation) - (Vandromme *et al.,* 2016; Chartin *et al.*, 2013; Grangeon *et al.*, 2017). The change in proxy values observed in the current research together with this increase of accumulation of organic matter characterized by high C/N ratios very likely occurred in response to these landscape modifications (Mackie *et al.*, 2005).

After this period of more intense management (after 1970) the MARorg, TOC and chlorophyll-a proxies increased following a statistically significant trend (Table 4). These results suggest a greater accumulation of autochthonous organic matter. MARorg values obtained in agricultural and abandoned catchments during the 2010-2017 period (255 ± 170 and 78 ± 22 gC m^{-2} yr^{-1}, respectively) are in agreement with those obtained in previous studies (Fig. 5). For example, a median value of 350 gC m^{-2} yr^{-1} and 56 gC m^{-2} yr^{-1} were respectively recorded in reservoirs draining cultivated and abandoned catchments - (Schlesinger & Bernhardt, 2013).

Regional trend

The compilation of results obtained in the seven agricultural catchments demonstrates the continuous acceleration in organic material accumulation in ponds across the Loire River basin during the 20th century (MK-test P <0.05). Similar observations were made in agricultural catchments of the northern United-States (Heathcote *et al.*, 2013). In this area, the regional acceleration started around 1950 and was accompanied by an increase of C/N ratios in sediment (Fig. 7). In previous paleolimnological studies, these increases were interpreted as historical periods characterized by the delivery of a high proportion of organic matter derived by soil erosion particularly during periods of greater human-induced environmental modifications (Guilizzoni *et al.*, 1996; Routh *et al.*, 2004). In addition to this change, $\delta^{15}N$ signature recorded a general decrease suggesting a major change in organic matter sources. The beginning of acceleration of organic matter deposits (1950) recorded in these reservoirs occurred concomitantly with the major landscape changes that took place in the Loire river basin. These changes were associated with an acceleration of erosion processes and a higher sediment delivery to the reservoirs (Foucher *et al.*, 2014). This period of soil erosion was observed in various catchments across Europe. For example, a two to ten-fold acceleration of soil erosion rates was recorded in various catchments of the UK after 1950 in response to land-use change (Foster *et al.*, 2011). In addition, the greater contribution of phytoplanctonic production was also observed from

1955 onwards: chlorophyll-a started to increase following the regional trends of N fertilizer inputs (r = 0.9 between chlorophyll-a contents and N inputs during the 1955-1990 period). From 1970 onwards, the terrigenous contribution decreased sharply following the trend of MARorg. After 1970, human pressure on landscape started to decrease in France (land consolidation programs mainly took place between 1955 and 1975, Andre & Polombo, 2013). After a period dominated by the terrigenous contribution to sediment deposited in the reservoirs, the MARorg showed a progressive acceleration from 1970 to 2015 (+40%). At the regional scale, $\delta^{15}N$ is well correlated to N inputs (r = 0.76), C/N ratio (r = 0.8), to MARorg after 1970 (r = 0.72) as well as to chlorophyll-a (r = 0.68). The increase of organic matter deposition associated with a good correlation between phytoplanctonic proxies demonstrates a shift in the paleo productivity evolving from a system dominated by terrigenous inputs just after WWII to a period of dominant autochthonous production after 1970.

Between 1990 and 2015, the European legislation induced a slight reduction in fertilizer use in the Loire river basin (-13% on average) - (Poisvert *et al.*, 2017). Nevertheless, organic matter continues to accumulate in reservoirs (+17% in 15 years). The MARorg remained highly correlated to phytoplanctonic proxies during this period (r = 0.87 between chlorophyll-a and MARorg). The negative correlation between N inputs and phytoplanctonic occurrence (r = 0.95 between chlorophyll-a and N inputs and r = 0.97 between MARorg and N inputs) highlights the effects of other driving factors and not only the trends in agricultural inputs. Past studies have demonstrated that in addition to human activities, climate warming or again secondary release of nutrients (Shayo & Limbu, 2018) may have a major impact on organic production and eutrophication phenomena.

Nowadays, although eutrophication represents a major threat for a large number of reservoirs across the world (Le *et al.*, 2010; Bhagowati & Ahamad, 2019), this process remains insufficiently studied in small headwater basins. The general positive trend of paleo production proxies observed in study could be improved by the collection of additional samples in various catchments of the Loire basin. Nevertheless, the results obtained in the current research emphasized the occurrence of a massive acceleration of organic matter deposition after 1950 in these reservoirs. Moreover, the sediment recorded in ponds draining contrasting land uses also showed a transition between a system dominated by terrigenous inputs to a system dominated by the autochthonous production during the

1950-2015 period. Although the paleo production proxies were highly correlated to the use of agricultural inputs until the 1990s, this relationship was no longer observed since then. Accordingly, questions remain to identify the factor(s) driving the recent autochthonous production in these reservoirs. Overall, soil erosion is classically considered to be the main factor inducing siltation of water bodies. As the excess of organic matter production can also lead to the filling of water bodies, the contribution of these processes and their respective contribution to reservoir siltation need to be further quantified. This will allow the design of effective control measures such as the systematic sowing of cover crops in winter to improve nutrient absorption by plants and better protect soils against erosion.

5. Conclusions

The collection and analysis of sediment accumulated in freshwater bodies provides a powerful technique for reconstructing changes in organic matter sources and for investigating their relationship with landscape management. Although these changes were studied during the 20th century in coastal areas, great lakes or during the last decades in riverine systems, there is currently a lack of records to support a regional analysis of these changes in continental areas over the last century. Results obtained in the current research underline an acceleration of organic matter deposition rates in cultivated areas during the second part of the 20th century. Between 1950 and 1965, organic matter that accumulated in water bodies draining agricultural catchments was mainly supplied by terrigenous sources. These deposits occurred during the implementation of major landscape management programs such as land consolidation, soil drainage or stream re-design. The increasing use of synthetic fertilizers which started in the 1970s induced a shift in organic matter accumulation with the acceleration of primary production in water bodies. This autochthonous production was highly correlated to the use of N fertilizers until the early 1990s. Nevertheless, the current research contributed to improve our understanding of long-term trends in eutrophication through the identification of a switch in production and the associated driving factors during the 1960-1970 period. Since then, although the primary production continues to increase, this change cannot be exclusively explained by the enhanced use of fertilizers. The other factors driving this change should therefore be identified and quantified. This identification is of prime importance in order to reduce primary production in these water bodies and to improve the water quality of freshwater systems.

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Figures:

Fig.1 Localization of the nine studied catchments within the Loire river basin. (1) Le Loroux-Bottereau, (2) Beaurepaire, (3) Passavant-sur-Layon, (4) Brosse, (5) Boisvinet, (6) Prugnolas, (7) Goule, (8) Tazenat, (9) Malaguet

Fig. 2 Evolution of sediment properties throughout time in reservoirs draining forested catchments: (6) Prugnolas and (9) Malaguet. Grey lines correspond to the identification of ^{137}Cs peaks associated to the 1963 and 1986 fallouts.

Fig. 3 Evolution of sediment properties throughout time in reservoirs draining catchments dominated by grassland: (1) Le Loroux-Bottereau, (2) Beaurepaire, (7) Goule and (8) Tazenat. Grey lines correspond to the identification of ^{137}Cs peaks associated to the 1963 and 1986 fallouts.

Fig. 4 Evolution of sediment properties throughout time in reservoirs draining catchments dominated by arable land: (3) Passavant-sur-Layon, (4) Brosse and (5) Boisvinet. Grey line correspond to the identification of ^{137}Cs peak associated to the 1963 fallouts.

Fig. 5 Evolution of Nitrogen consumption in the nine selected catchments under arable land, grassland or dominated by forest (1) Le Loroux-Bottereau, (2) Beaurepaire, (3) Passavant-sur-Layon, (4) Brosse, (5) Boisvinet, (6) Prugnolas, (7) Goule, (8) Tazenat, (9) Malaguet

Fig. 6 Evolution of Mass Accumulation Rates of organic material (MARorg) during the last century in reservoirs located at the outlet of the nine studied catchments: (1) Le Loroux-Bottereau, (2) Beaurepaire, (3) Passavant-sur-Layon, (4) Brosse, (5) Boisvinet, (6) Prugnolas, (7) Goule, (8) Tazenat, (9) Malaguet. Grey area correspond to a significant acceleration of MARorg.

Fig. 7 Evolution of sediment properties throughout time in reservoirs draining the seven cultivated catchments. The light grey part corresponds to the period dominated by terrigenous inputs whereas the dark grey colour corresponds to the period dominated by autochthonous primary productivity.

Tables:

Table 1. Characteristics of the Loire Basin sub-catchments

Table 2. Characteristics of the studied catchments

Table 3. Chronology of sediment cores and modern and historic Mass Accumulation Rates of organic matter (MARorg expressed in gC m^{-2} yr^{-1}: modern MARorg correspond to average value of MARorg for the 2017-1950 period and the historical MARorg to the average value before 1950). ND = non detected.

Table 4. Results of the Mann Kendal test with the significant *p* value <0.05. NT = No trend, + = positive trend and - = negative trend

	Sub catchment area (km²)	Average elevation (m)	Average slope (%)	Land use
Lower Loire	36,780	108	1.7	Arable land (60%), Grassland (24%), Forest (11%), Urban (5%)
Middle Loire	48,471	216	2.1	Arable land (48%), Forest (25%), Grassland (24%), Urban (4%)
Upper Loire	32,630	570	5.5	Grassland (43%), Forest (35%), Arable land (17%), Urban (4%)

Tables

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Site ID	Reservoir name	Core location	Core length (cm)	Water depth (m)	Lake/Pond area (ha)	Catchment area (km^2)	Average elevation (m)	Average slope (%)	Catchment location	Main land use	Land use	Landscape management
1	Loroux-Botterau	47.2379N, -1.3440E	71	1.2	1.7	4.5	68	2.7	Lower Loire	Grassland (65%)	Arable land (34%). urban area (1%)	Hedge removal during the 1965-1975 period
2	Beaurepaire	47.0726N, -0.4737E	108	2.5	38	14.3	122	1.7	Lower Loire	Grassland (52%)	Arable land (45%). water bodies (3%). woodland (0.1 %)	tile drain implementation and land consolidation in 1977
3	Passavant-sur-Layon	47.1013N, -0.3941E	116	1.4	14	108	121	2.4	Lower Loire	Arable land (70.5%)	Grassland (21%). woodland (6.36%). water bodies (0.9%). mining (0.6%). urban areas (0.3%)	Major land consolidation during the 1960's
4	Brosse	47.2761N, 1.0558E	127	2.4	11	24.5	105	2.3	Middle Loire	Arable land (83%)	Woodland (8%). grassland (7%). water bodies (1%). urban areas (1%)	Major land consolidation in 1959
5	Boisvinet	48.0733N, 0.8832E	97	2.1	39	9.5	189	2.5	Lower Loire	Arable land (63%)	Grassland (23%). woodland (9.5%). water bodies (4.3%)	
6	Prugnolas	45.8689N, 1.9032E	82	0.8	1.8	7.8	727	12	Middle Loire	Woodland (82%)	Grassland (16%). arable land 0.4%)	Afforestation after 1950, major windstorm in 1999 inducing damage on forest
7	Goule	46.7277N, 2.8004E	152	4.3	52	34	242	3	Middle Loire	Grassland (65.9%)	Woodland (18.4%). arable land (13.3%). water bodies (1.5%). urban areas (0.8%)	
8	Tazenat	45.9796N, 2.9900E	115	67	30	2.3	690	9.3	Upper Loire	Grassland (68%)	Woodland (16%). water bodies (15%)	Land consolidation in 1990
9	Malaguet	45.2512N, 3.7103E	69	3.1	20.5	3.7	1073	7.5	Upper Loire	Woodland (71%)	Grassland (13%). water bodies (7%). urban areas (6%). arable land (2%)	Afforestation works between 1950 and 1965

Site ID	Max $^{210}Pb_{ex}$ date / depth	1986 ^{137}Cs fallout	1963 ^{137}Cs fallout	Modern MARorg		Historic MARorg	
1	1921 (71 cm)	ND	± 3 year (40 cm)	133	± 32	46	± 21
2	1925 (105 cm)	ND	± 2 year (70 cm)	219	± 71	76	± 12
3	<100 (74 cm)	ND	± 2 year (46 cm)	229	± 50	133	± 11
4	1922 (130 cm)	ND	± 2 year (92 cm)	460	± 117	342	± 126
5	1898 (90 cm)	ND	± 3 year (50 cm)	111	± 28	76	± 2
6	1918 (140 cm)	± 1 year (55 cm)	± 1 year (85 cm)	167	± 12	114	± 25
7	1901 (65 cm)	± 1 year (11.5 cm)	ND	141	± 46	450	± 330
8	1902 (44 cm)	± 1 year (11 cm)	± 3 year (19 cm)	41	± 11	21	± 12
9	1948 (76 cm)	± 4 year (16 cm)	ND	163	± 73	-	

Site ID	TOC		$\delta^{13}C$		$\delta^{15}N$		C/N		TN		chloropyll-a		MARorg		N Inputs	
1	0.46	NT	<0.05	-	<0.05	-	<0.05	-	0.46	NT	<0.05	+	<0.05	+	<0.05	+
2	<0.05	+	<0.05	-	<0.05	+	0.3	NT	<0.05	+	<0.05	+	<0.05	+	<0.05	+
3	<0.05	+	<0.05	-	<0.05	+	0.27	NT	<0.05	-	<0.05	+	0.53	NT	<0.05	+
4	0.84	NT	0.82	NT	0.07	NT	0.11	NT	0.96	NT	<0.05	+	0.33	NT	<0.05	+
5	<0.05	+	0.6	NT	<0.05	+	0.46	NT	<0.05	+	<0.05	+	<0.05	+	0.43	NT
6	<0.05	+	<0.05	-	0.19	NT	<0.05	-	<0.05	+	<0.05	+	<0.05	+	<0.05	+
7	0.138	NT	0.408	NT	<0.05	-	0.5	NT	<0.05	+	0.06	NT	<0.05	-	0.38	NT
8	<0.05	+	<0.05	-	0.54	NT	0.46	NT	<0.05	+	0.38	NT	<0.05	+	<0.05	+
9	0.13	NT	<0.05	-	0.45	NT	0.23	NT	<0.05	+	<0.05	+	<0.05	-	<0.05	-

Figure 1
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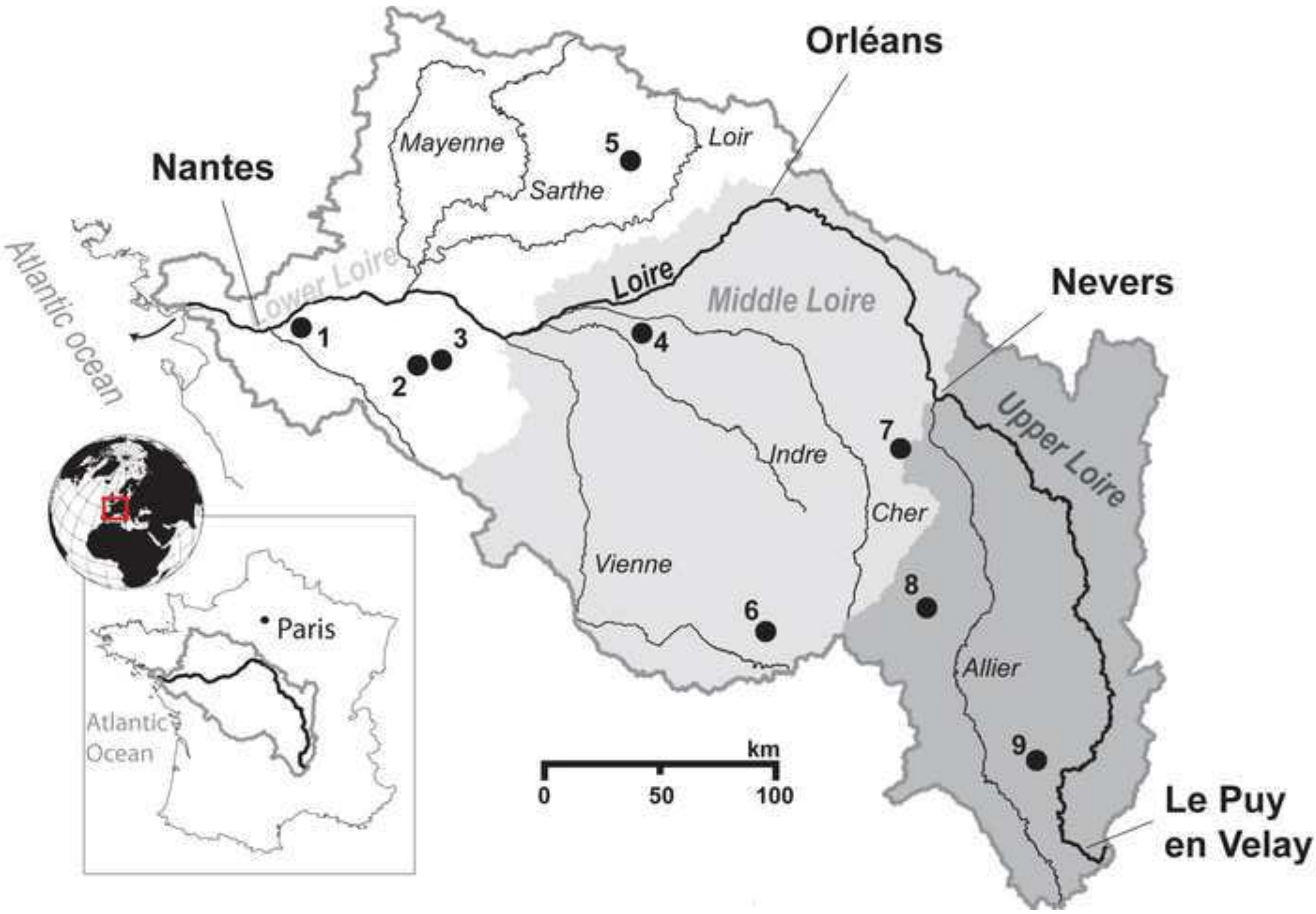

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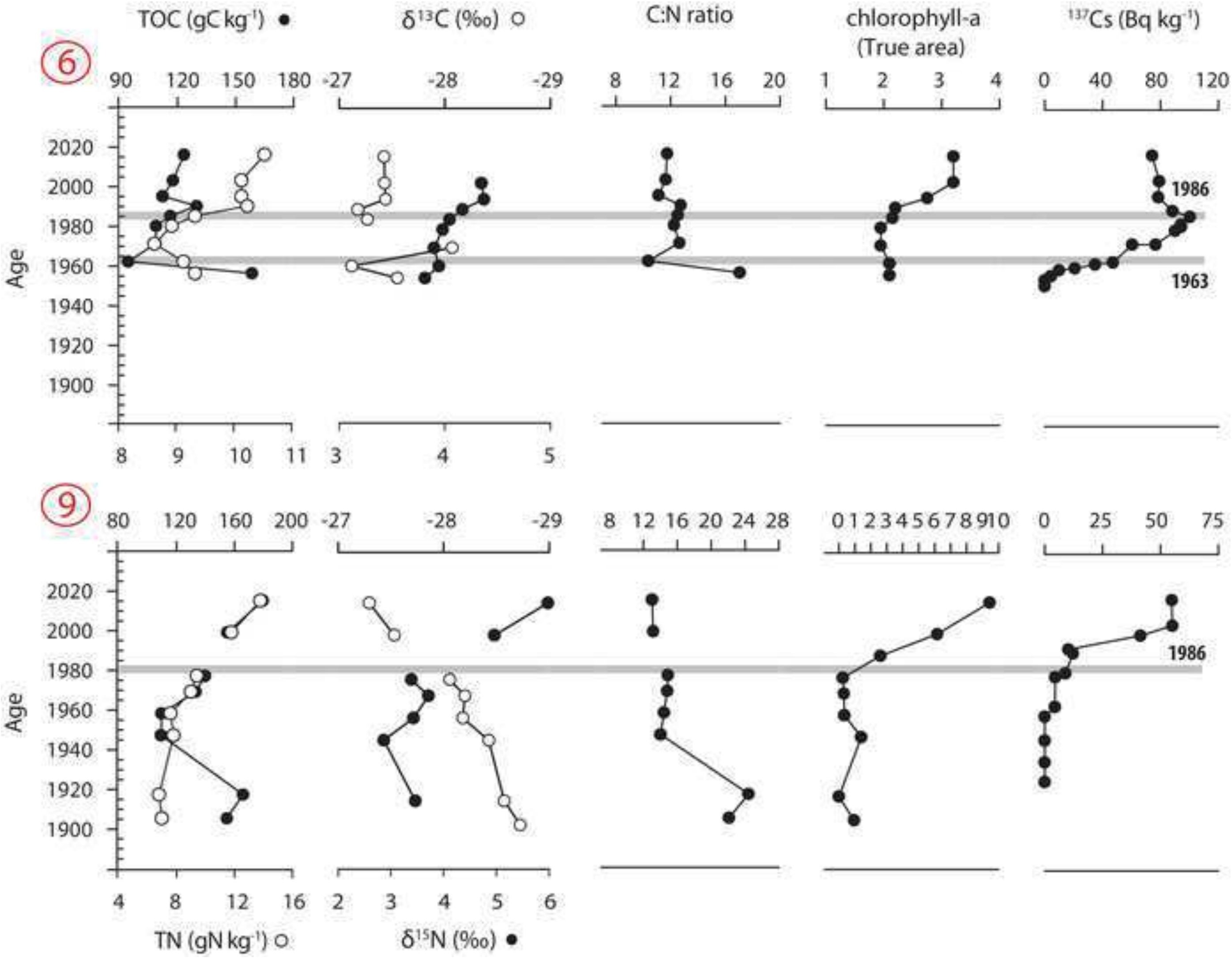

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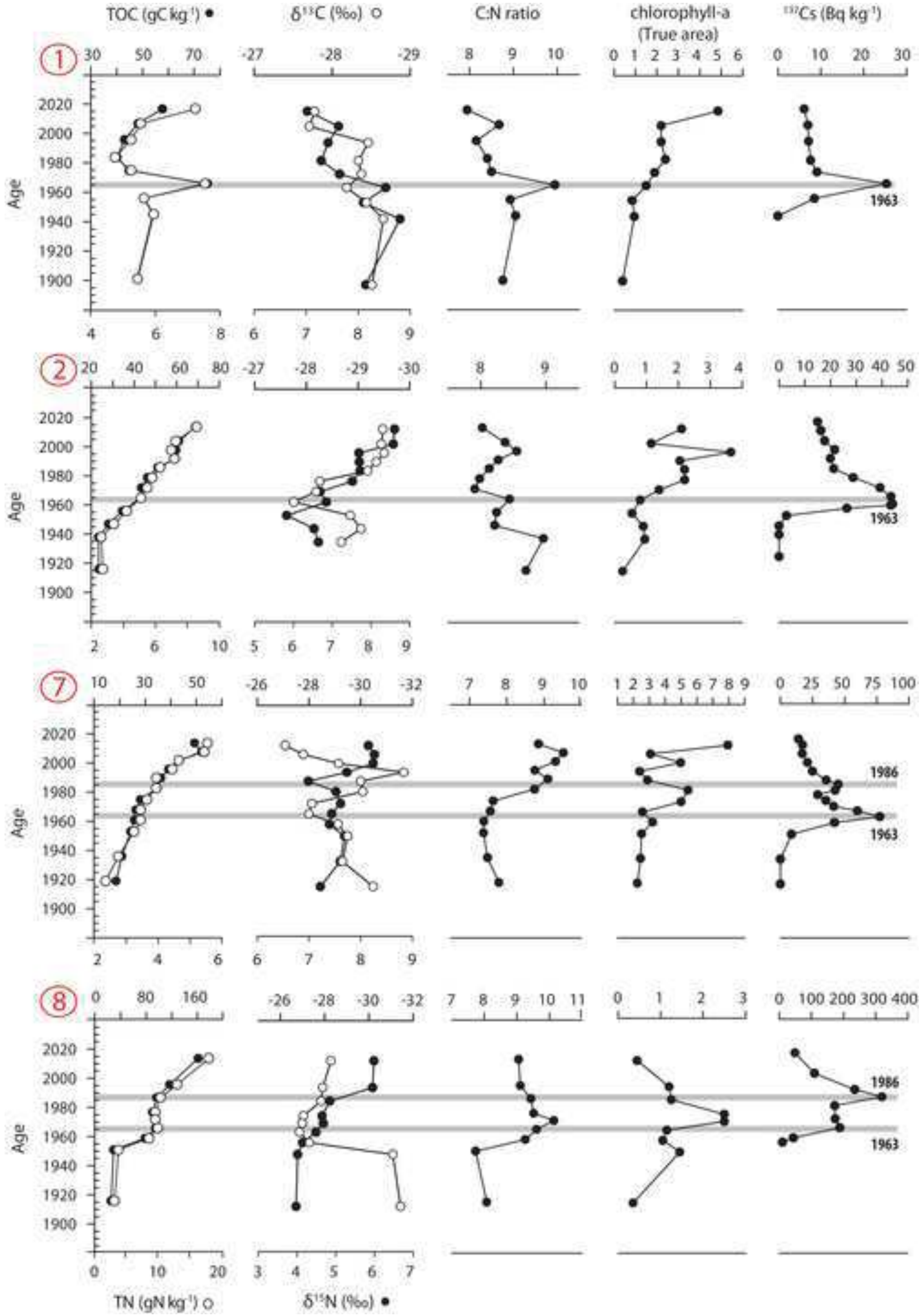

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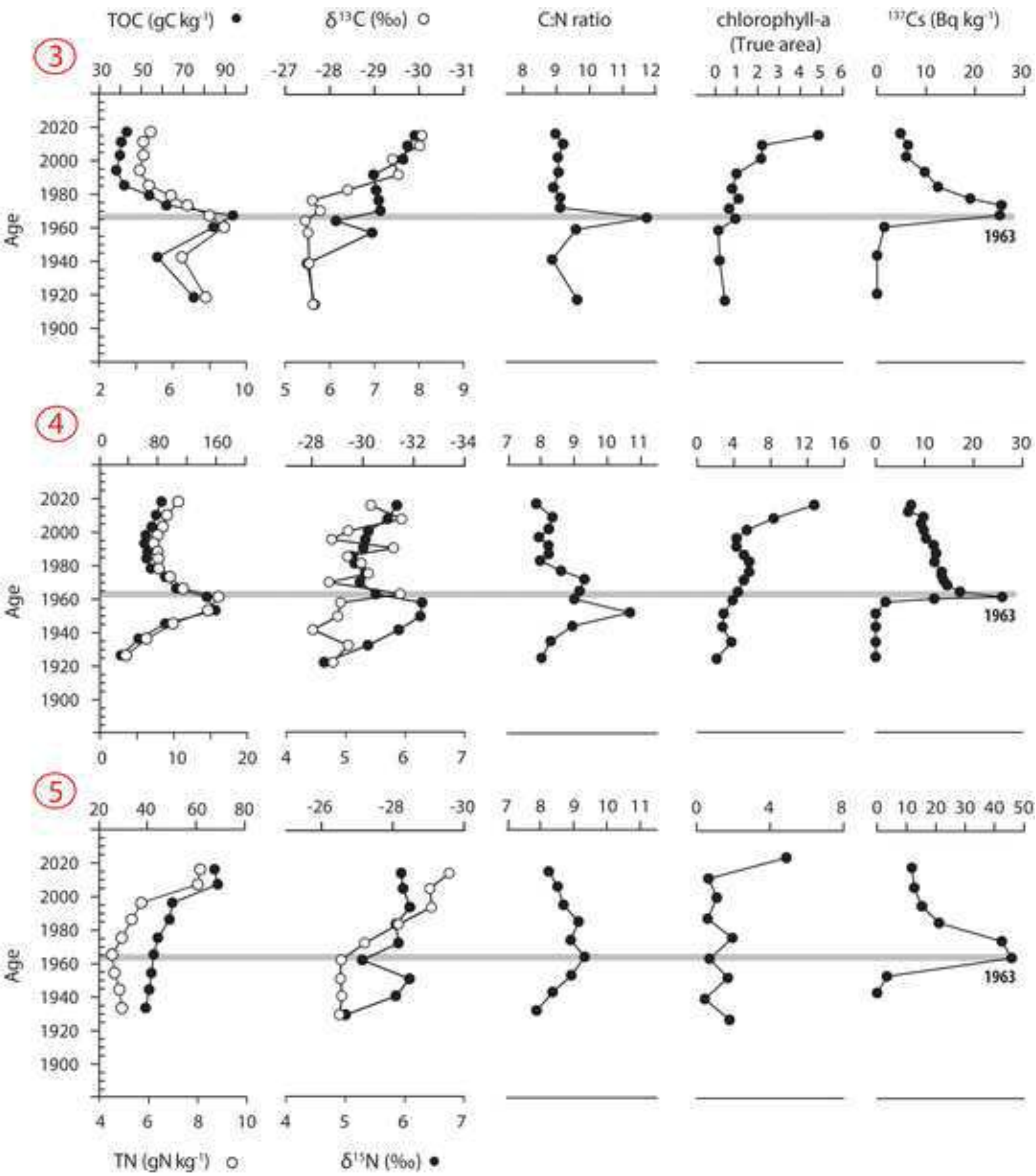

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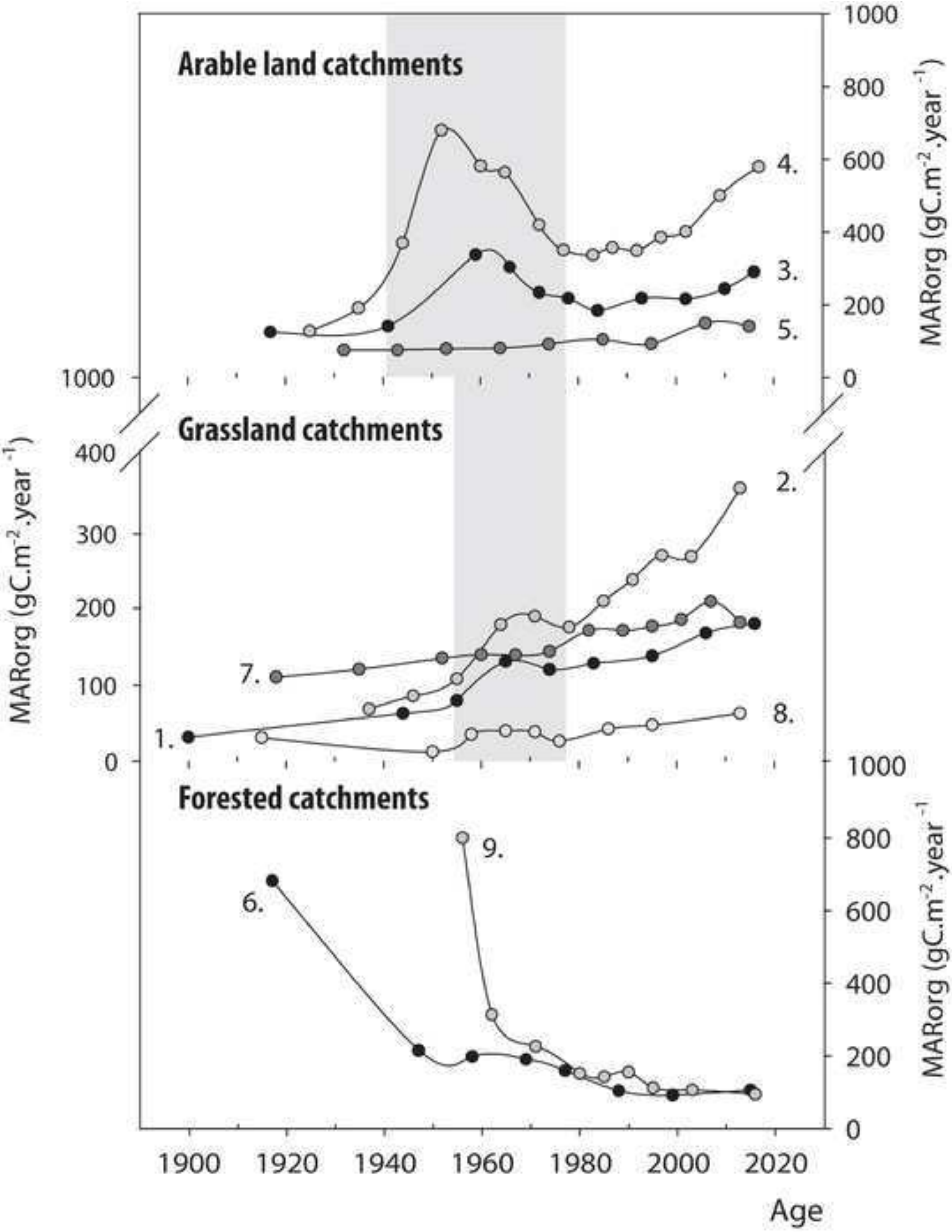

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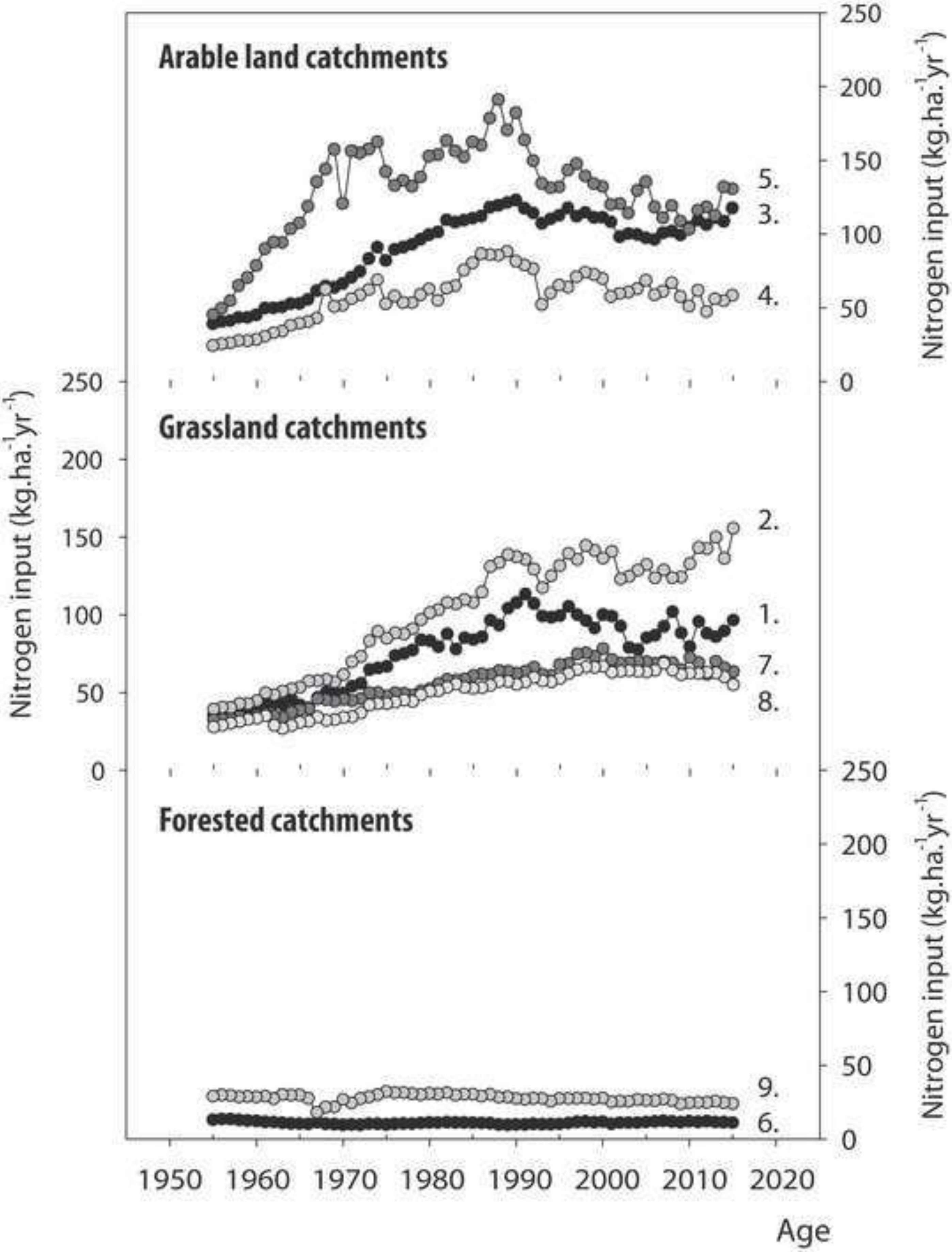

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