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Quantifying sediment sources in a lowland agricultural catchment pond using ^{137}Cs activities and radiogenic ^{87}Sr/^{86}Sr ratios

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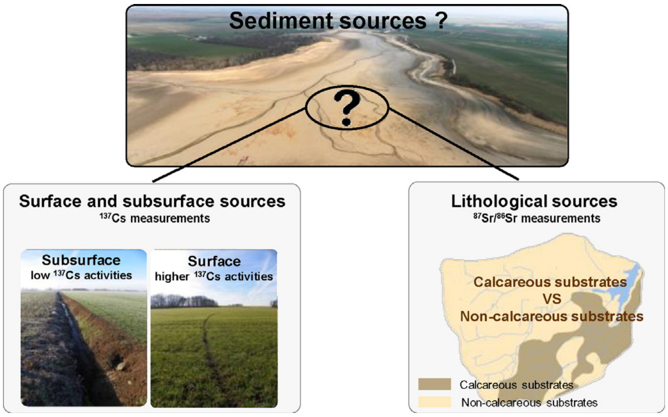
HIGHLIGHTS

- Surface sources supplied the majority of pond and core sediment.
- Lithological sources were well mixed in surface pond sediment.
- Lithological sources varied through time in the sediment core.
- Temporal lithological fluctuations likely resulted from landscape modifications.
- Understanding sediment dynamics is important in agricultural drained catchments.

GRAPHICAL ABSTRACT



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ABSTRACT

Soil erosion often supplies high sediment loads to rivers, degrading water quality and contributing to the siltation of reservoirs and lowland river channels. These impacts are exacerbated in agricultural catchments where modifications in land management and agricultural practices were shown to accelerate sediment supply. In this study, sediment sources were identified with a novel tracing approach combining cesium (^{137}Cs) and strontium isotopes (^{87}Sr/^{86}Sr) in the Louroux pond, at the outlet of a lowland cultivated catchment (24 km^2, Loire River basin, France) representative of drained agricultural areas of Northwestern Europe.

Surface soil ($n = 36$) and subsurface channel bank ($n = 17$) samples were collected to characterize potential sources. Deposited sediment ($n = 41$) was sampled across the entire surface of the pond to examine spatial variation in sediment deposits. In addition, a 1.10 m sediment core was sampled in the middle of the pond to reconstruct source variations throughout time. ^{137}Cs was used to discriminate between surface and subsurface sources, whereas ^{87}Sr/^{86}Sr ratios discriminated between lithological sources. A distribution modeling approach quantified the relative contribution of these sources to the sampled sediment.

Results indicate that surface sources contributed to the majority of pond (μ 82%, σ 1%) and core (μ 88%, σ 2%) sediment with elevated subsurface contributions modeled near specific sites close to the banks of the Louroux pond. Contributions of the lithological sources were well mixed in surface sediment across the pond (i.e., carbonate sediment contribution, μ 48%, σ 1% and non-carbonate sediment contribution, μ 52%, σ 3%) although there were

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significant variations of these source contributions modeled for the sediment core between 1955 and 2013. These fluctuations reflect both the progressive implementation of land consolidation schemes in the catchment and the eutrophication of the pond.

This original sediment fingerprinting study demonstrates the potential of combining radionuclide and strontium isotopic geochemistry measurements to quantify sediment sources in cultivated catchments.

1. Introduction

Soil erosion is a major environmental threat worldwide. This process of detachment, transportation and deposition of soil particles by rainfall and runoff particularly affects agricultural areas of Northwestern Europe (Boardman, 1993; Evrard et al., 2007; Le Bissonnais et al., 2005). Soil erosion not only results in decreasing soil fertility and crop yields (Bakker et al., 2004; Boardman et al., 2003), it often supplies high sediment loads to river networks (Owens et al., 2005).

High suspended sediment loads may increase turbidity and result in the sedimentation of downstream reservoirs and lowland river channels (Devlin et al., 2008; Vörösmarty et al., 2003). Sediment may also transport nutrients and contaminants including phosphorous, pesticides, persistent organic pollutants, heavy metals, pathogens and radionuclides (Ayrault et al., 2012; Chartin et al., 2013; Gateuille et al., 2014; Horowitz, 2008). Therefore, understanding spatial and temporal variations of sediment sources is useful for managing the supply of sediment and contaminants in river systems.

Agricultural landscapes have been extensively modified by human activities during the last century to facilitate mechanization and increase crop yields (Dotterweich, 2013; García-Ruiz, 2010; Valentin et al., 2005). In wetlands, tile drain outlets have been installed and channels have been created to evacuate excess water. Although these alterations resulted in substantial increases in soil erosion and downstream sediment loads, there has been limited research quantifying erosion and sediment transport in these areas (Foucher et al., 2014; Russell et al., 2001; Sogon et al., 1999; Walling et al., 2002). Furthermore, even fewer studies (e.g. Russell et al., 2001) have examined the relative contribution of different sediment sources in these drained lowland agricultural catchments.

Quantifying sediment sources is important to target efficient management measures that reduce sediment supply in catchments. Sediment fingerprinting techniques are therefore increasingly applied to determine sediment sources and pathways in catchments and thus inform management interventions (Collins and Walling, 2002; Koiter et al., 2013; Walling, 2005). Sediment fingerprinting techniques often trace radionuclide, geochemical, and mineralogical soil and sediment properties (Collins et al., 2012; Evrard et al., 2016; Evrard et al., 2011; Olley et al., 1993; Walling et al., 2008). Sediment color or infrared spectroscopy (Martínez-Carreras et al., 2010; Poulenard et al., 2012), plant pollen (Brown et al., 2008), soil enzymes (Nosrati et al., 2011), sediment magnetic properties (Hatfield and Maher, 2009; Hatfield et al., 2008) or methyl esters (Banowetz et al., 2006) have also been used to discriminate between potential sediment sources. For a review of the strengths and limitations of different tracer properties and tracing approaches, please see Collins and Walling (2004), Davis and Fox (2009), Guzmán et al. (2013), Haddadchi et al. (2013), and Koiter et al. (2013).

The choice of discriminant properties is often guided by the sources supplying sediment. For example, fallout radionuclides discriminate between surface and subsurface sources (Owens and Walling, 2002; Smith and Dragovich, 2008). ^{137}Cs ($t_{1/2} = 30$ years) is an artificial radionuclide, produced by thermonuclear tests in the 1950s and 1960s, the Chernobyl accident that affected Northwestern Europe in 1986 and the Fukushima Dai-ichi Nuclear Power Plant accident in 2011. Radiocesium is strongly bound to fine particles (He and Walling, 1996). In undisturbed soil profiles, ^{137}Cs concentrations are the highest at the surface before decreasing exponentially with depth (Mabit et al., 2008; Olley et al., 2013). Accordingly, sediment originating from the soil surface or the ploughed layer will contain higher ^{137}Cs concentrations compared to sediment originating from subsurface sources (e.g. channel bank and gully erosion), which will be depleted in ^{137}Cs. Therefore, it is possible to quantify the relative contribution of surface and subsurface sources by modeling ^{137}Cs soil and sediment concentrations (Caitcheon et al., 2012; Olley et al., 2013).

In comparison, strontium isotopes (^{87}Sr/^{86}Sr) were shown to be effective tracers of water, soil, sediment and biological material in the environment as they are not fractionated by chemical or biological processes (Aberg, 1995; Graustein, 1989). The abundance of ^{87}Sr produced by the radioactive decay of ^{87}Rb (expressed as the ^{87}Sr/^{86}Sr ratio) varies with rock type and its formation age (Négrel and Roy, 1998; Yasuda et al., 2014). Accordingly, strontium isotopic ratios reflect catchment lithology and thus they have been used to trace the geological sources of soils, suspended particulate matter and riverine water in catchments (Faure, 1986).

Strontium isotopic ratios have mainly been measured in the dissolved load (Gaillardet et al., 1997; Grosbois et al., 2000; Pande et al., 1994) to identify and quantify chemical weathering fluxes in major rivers (e.g. the Amazon, Congo, Garonne, Indus, Loire, Rhine Rivers catchments) and to provide information about surface and subsurface water circulations (Bakari et al., 2013; Brenot et al., 2008; Eikenberg et al., 2001; Petelet-Giraud et al., 2007), water-rock interactions (Aubert et al., 2001; Blum et al., 1994) or seawater dynamics (Jørgensen et al., 2008). Strontium isotopic ratios were also measured in suspended matter to identify the sources of particles transported in the ocean (Asahara et al., 1999; Goldstein and Jacobsen, 1988), in estuarine (Douglas et al., 2003; Smith et al., 2009) and fluvial systems (Asahara et al., 2006; Douglas et al., 1995; Négrel and Grosbois, 1999; Viers et al., 2000; Wasson et al., 2002). Despite their use in investigations of particulate material dynamics at large catchment scales, few studies investigated spatial and temporal variations of sediment sources with strontium isotopic ratios in small agricultural catchments (<50 km^2). Small catchment scale research is important for improving our understanding of the impact of land use and farming practice changes on sediment dynamics.

In this study, sediment sources are identified and quantified through the combination of ^{137}Cs and ^{87}Sr/^{86}Sr ratio measurements on soil and sediment collected in the Louroux catchment (24 km^2 - Loire River basin, France), representative of drained, lowland, cultivated areas of Northwestern Europe. The Louroux pond, at the catchment outlet, is significantly impacted by sedimentation from increased sediment yields. Intense modifications in agricultural practices and land use in the catchment resulted in the excessive transport of fine sediment that was predominantly deposited in the Louroux pond. Fine sediment also transfers particulate-bound nutrients and contaminants and degrades water quality. As water quality may be directly impacted by this excess supply of sediment in this catchment, research is required to better understand sediment source dynamics in order to meet the requirements of the EU Water Framework Directive.

In this agricultural catchment, sediment surface sources were defined as topsoil material eroded from the cropland whereas subsurface sources were defined as material eroded from channel banks. Surface sources were shown to dominate (99 ± 1%) the supply of suspended matter transiting this catchment's rivers during flood events in 2013 (Foucher et al., 2015). However, the dominance of surface source contributions to sediment deposited throughout the pond and over a longer temporal period requires further investigation. Furthermore, information on the main spatial sources of sediment in the Louroux pond is required. To investigate spatial and temporal variations in sediment sources, ^{137}Cs concentrations and ^{87}Sr/^{86}Sr ratios were measured to estimate the relative contributions of surface, subsurface and lithological sources to multiple short sediment cores (i.e. <10 cm) sampled throughout the Louroux pond as well one long sediment core (i.e. 1.1 m) sampled in the central pond depression.

2. Material and methods

2.1. Study site

The Louroux catchment (24 km^2) is a small agricultural lowland basin with elevation ranging between 99 and 127 m and a mean slope of 0.4%. The climate is temperate oceanic with a mean annual rainfall of 696 mm (Tours, data from Météo France, 2015). Cropland is the main land use (78%) followed by grassland (18%) and woodland (4%) (Corine Land Cover 2006 data). According to a geological survey, the lithology consists of post-Helvetian sand and continental gravels (32%), Senonian flint clays (23%), Quaternary loess (18%), Helvetian shelly sands (18%), Ludian Touraine lacustrine limestones (6%) and Eocene silicic conglomerates (2%) (Fig. S1) (Rasplus et al., 1982). These lithologies were regrouped in two classes (Le Gall et al., 2016): a southern carbonate area composed of Touraine Lacustrine limestone and shelly limestone, and a northern non-carbonate grouping of the remaining lithologies (Fig. 1a).

In the Louroux catchment, land consolidation started in the 1950s. Channels were created and others modified >220 tile drain outlets were installed to drain soils and facilitate intensive crop farming. As a result, soil erosion and sediment fluxes strongly increased, contributing to the siltation of the river network, the Beaulieu pond (3 ha – nearly filled), and the Louroux pond (52 ha) (Fig. 1c). Foucher et al. (2014) showed that terrigeneous inputs to the Louroux pond reached maximum rates of 2100 t km^{-2} yr^{-1} between 1945 and 1960, before decreasing to lower rates (90–102 t km^{-2} yr^{-1}) since 2000.

2.2. Sampling

2.2.1. Soil and channel bank sampling

Soil and channel bank samples were collected between January 2013 and April 2014. Sampling concentrated on cropland, as soil erosion was shown to be negligible under grassland and forest in similar environments (Cerdan et al., 2010). Surface sources ($n = 36$) were collected by scraping the top 2–3 cm layer of soil and subsurface sources ($n = 17$) by scraping a 2–3 cm layer of the sidewall from eroding channel banks (Fig. 1b). Each of these surface and subsurface source samples was composed of five sub-samples. A plastic spatula was used to collect samples and avoid potential metal contamination.

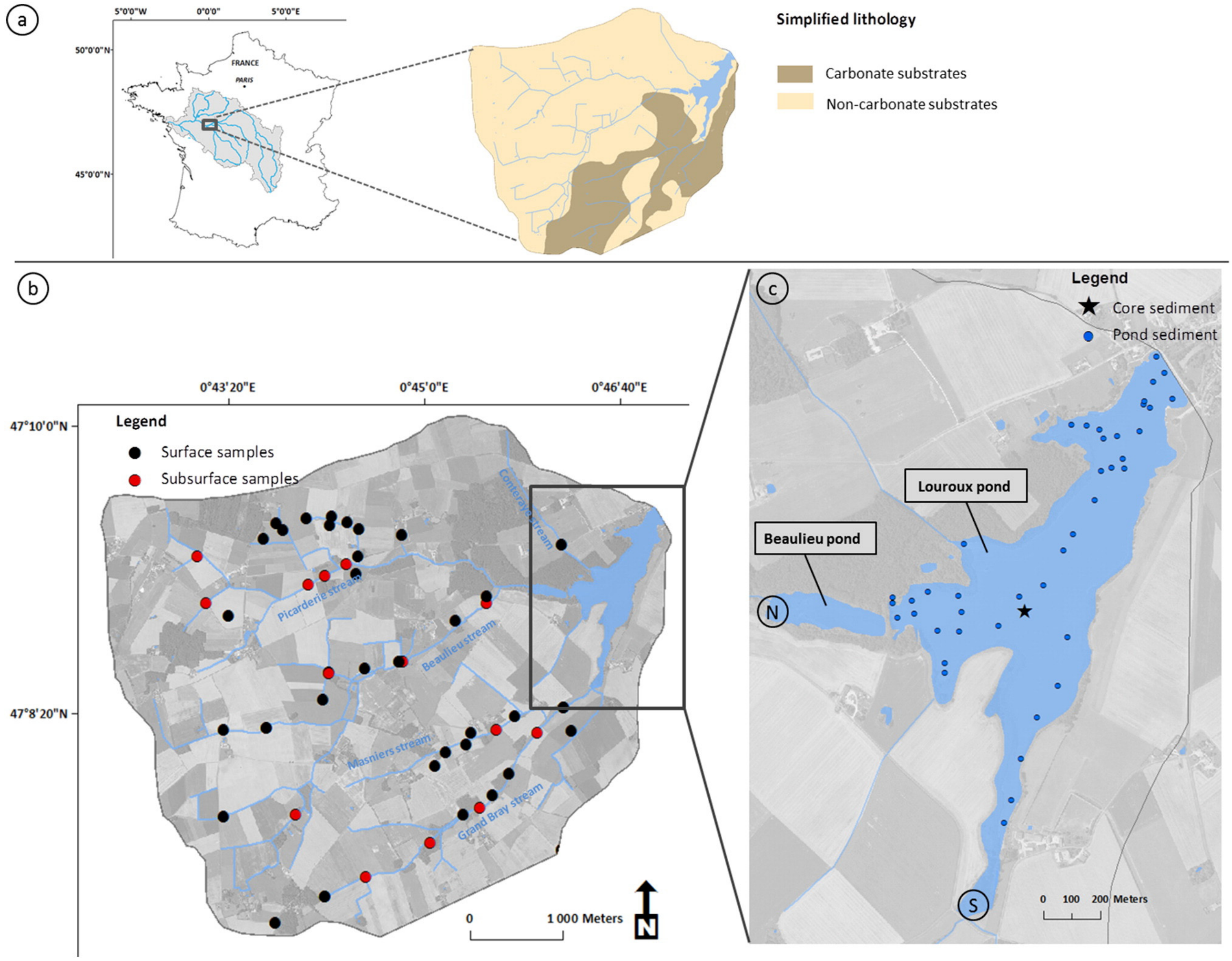

Fig. 1. Map of the Louroux catchment in the Loire River basin (France) along with the simplified lithological map of the area (Le Gall et al., 2016) (a) and the locations of surface and subsurface source (b), pond and core sediment (c) sample locations. N and S correspond to the northern and southern inlets of the main tributaries.

2.2.2. Louroux pond sediment sampling

Surface samples of deposited pond sediment (n = 41) were collected in September 2012 using a floating platform and a short (top 0–10 cm) gravitational corer UWITEC (Ø 90 mm) during a period of low water level (see graphical abstract). Attention was paid to collect the most recent deposits following a random location sampling technique. A longer sediment core was collected in the central depression of the pond (1.10 m length) in March 2013, at the confluence between the Grand Bray and Beaulieu streams (Fig. 1c). The sediment core was dated in a previous study using an age depth model based on fallout radionuclide measurements (^{137}Cs and ^{210}Pb$_{xs}$) (Foucher et al., 2014). In the remainder of the text, dates attributed to the successive sediment core layers are used to facilitate the interpretation of the core results. Carbonate outcrops (n = 3), shelly sand (n = 1), and three types of fertilizers (N, 33.5/P.K, 25–25/N.P.K, 15–15–15) commonly used by farmers in this catchment were also sampled to characterize their strontium isotopic signatures.

2.3. Sample processing and laboratory analysis

2.3.1. Gamma spectrometry measurements

Soil (n = 36), channel bank (n = 17) and sediment (n = 41) samples were dried at 40 °C and sieved to 2 mm before analysis. For radionuclide measurements, approximately 80 g of material was analyzed. ^{137}Cs (662 keV) activities were determined by gamma spectrometry using low background N and P type GeHP detectors (Canberra and Ortec) at the Laboratoire des Sciences du Climat et de l'Environnement. Measured activities were decay-corrected to the sampling date and provided with 2σ-errors. Th concentrations (mg kg^{-1}) were calculated from ^{228}Th activity concentrations. Assuming that ^{232}Th and its daughter products were in secular equilibrium, ^{228}Th activities were calculated using the average between the gamma rays of two of its daughter products, ^{212}Pb (239 keV) and ^{208}Tl (583 keV). Counting efficiencies and reliability were conducted using certified International Atomic Energy Agency (IAEA) standards (IAEA-444, 135, 375, RGU-1 and RGTh-1) prepared in the same containers as the samples. Uncertainties on radionuclides activities were ca. 5% for ^{228}Th, and up to 10% for ^{137}Cs. Based on ^{228}Th activities, the total Th concentration (mg kg^{-1}) of sediment samples was calculated using the universal law of radioactive decay.

2.3.2. Thorium particle size correction for ^{137}Cs activities

As ^{137}Cs is strongly bound to fine particles, potential particle size differences between sources and sediment may prevent their direct comparison. To avoid errors in the estimation of source contributions, the impacts of particle size on sediment properties must be carefully addressed. As an alternative to a specific surface area (SSA) derived correction, a thorium correction was effectively applied by Foucher et al. (2015) in the Louroux pond catchment. These authors demonstrated that thorium-corrected particle size corrections produced globally better results compared to SSA corrections in this catchment.

The Th correction factor was calculated based on the variations of Th and ^{137}Cs concentrations in each sediment sample and each source sample (Eq. (1)) compared to the mean Th and ^{137}Cs concentrations of the considered source.

$$Th\ sedimentcorrectionfactor = \frac{[Th]_{i,j} \Big/ [Th]_{meansource(s)}}{\left[{}^{137}Cs\right]_{i,j} \Big/ \left[{}^{137}Cs\right]_{meansource(s)}} \tag{1}$$

where $[Th]_i$ and $[^{137}Cs]_i$ are the respective thorium and cesium concentration of each individual sediment sample (i), and $[Th]_{\text{mean source(s)}}$ and $[^{137}Cs]_{\text{mean source(s)}}$ are the respective thorium and cesium concentrations of both surface and subsurface samples when applied to each sediment sample while $[Th]_j$ and $[^{137}Cs]_j$ are the respective thorium and cesium concentrations of each individual source sample (j) (i.e. surface or subsurface samples) and $[Th]_{\text{mean source(s)}}$ and $[^{137}Cs]_{\text{mean source(s)}}$ are the respective thorium and cesium mean concentrations of each source when respectively applied to surface and subsurface samples. Corrected ^{137}Cs concentrations were calculated by dividing each measured ^{137}Cs concentration of each individual sample by the associated Th correcting factor.

2.3.3. Geochemical measurements

A selection of 31 surface sediment samples and 20 core sediment samples were analyzed for strontium isotopes. As recommended in several sediment fingerprinting studies (Collins and Walling, 2002; Motha et al., 2003; Tiecher et al., 2016; Walling et al., 2000), geochemical measurements were performed on the < 63 μm fraction of material, obtained by dry-sieving. Sieving samples to the < 63 μm fraction theoretically allows for a more direct comparison between sediment and potential sources elemental concentrations, as it is assumed that this size fraction corresponds to the bulk of the sediment.

2.3.3.1. Mineralization and selective extraction of the "exchangeable and carbonate" fraction. Details of the mineralization of source, sediment, carbonate rocks and fertilizer samples are given in Supplementary Material. Approximately 100 mg or 125 mg of material was dissolved by the successive addition of HF (47–51%), $HClO_4$ (65–71%), HCl (34–37%) and HNO_3 (67%) in closed Teflon vessels on hot plates. Proportions of reagents used and durations varied according to the sample nature.

Selective extractions using diluted acetic acid (F1 fraction of the BCR protocol) were performed to characterize the ^{87}Sr/^{86}Sr signature and composition of the exchangeable/carbonate fraction of sediment samples (Pueyo et al., 2001). Selective extractions of the exchangeable and carbonate phase (F1) were performed to evaluate the amount of calcium extracted and to characterize the ^{87}Sr/^{86}Sr signature of the exchangeable/carbonate fraction of sediment samples. This fraction corresponds to the metals affected by sorption and desorption effects (bound to particles) and/or (the elements) associated with carbonates. The selective extraction procedure was adapted from the BCR protocol (Rauret et al., 1999). 20 mL of a solution of acetic acid (0.11 mol L^{-1}) was added to approximately 500 mg of sediment in a centrifuge tube and was shaken for 16 h at room temperature. The extractant solution was separated from the residue by centrifugation (4000 rpm min^{-1} during 20 min) and stored at 4 °C before analysis. Reproducibility of the extraction was controlled through triplicate analyses of core sediment samples (n = 8). These sediment samples were selected to cover the ^{87}Sr/^{86}Sr ratio variations observed in the < 63 μm fraction of all core sediment samples. Results will be presented as the average strontium concentrations and ^{87}Sr/^{86}Sr ratios measured for each triplicate.

2.3.3.2. Elemental concentrations and strontium isotopic analyses. Major and trace element concentrations (Na, Mg, K, Ca, Rb, Sr, Zn) were analyzed in mineralized solutions using an inductively coupled plasma quadrupolar mass spectrometer (ICP-QMS) (X-Series, CCT II^{+} Thermoelectron, France). Internal standards (Re, Rh and In; SPEX, SCP Science, France) were used to correct for instrumental drift and plasma fluctuation. To limit interference, analysis was performed using a collision cell technology (CCT) which introduces a supplementary gas mixture of H_2 (7%) and He (93%) for the determination of Zn, Rb, and Sr concentrations.

A certified river water sample (SRM 1640a, NIST, Gaithersburg, USA) was used to control the ICP-MS calibration. The overall quality of ICP-MS measurements was controlled by analyzing a certified lake sediment material (IAEA lake sediment SL1). These standards were checked routinely during analysis (every 15–25 samples). Good agreement was observed between the data obtained and the certified values (n = 91 for SL-1 measurements). In the particulate compartment, analytical uncertainties did not exceed 10% (except for Ca, with a maximum analytical error of 13%).

Chemical separation of strontium from rubidium and calcium was performed using a cation-exchange procedure. More details are given in Supplementary Material. ^{87}Sr/^{86}Sr ratios were determined using a Thermo Finnigan Neptune-Plus Multi-collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS). The purified strontium fractions were diluted with 0.5 N HNO_3, adjusting the strontium concentration to 20 μg/L. The reproducibility of the ^{87}Sr/^{86}Sr ratio measurements was evaluated through replicate analyses of the NBS 987 standard. An average value $0.710306 \pm 10 \times 10^{-6}$ (2σ, $n = 92$) was obtained. Ratios were normalized to the NBS 987 standard value of 0.710245.

2.4. Mineralogical characterization (SEM-EDS and X-ray diffraction)

The mineralogy of a selection ($n = 7$) of surface and core sediment was characterized by scanning electron microscopy (SEM) at Geosciences Paris Sud (GEOPS). Thin sections of powdered material were mounted on a carbon sample-holder, coated with carbon and observed with a Phenom ProX scanning electron microscope using an accelerating voltage of 15 keV coupled with an X-ray energy dispersive spectral analyzer for element discrimination.

In addition, core sediment was characterized by X-ray diffraction (XRD) using Cu Kα radiation on powdered core samples. Diffractograms were recorded from 4° to 80° 2θ, under a voltage of 45 kV and an intensity of 40 mA using a PANalytical X'Pert PRO diffractometer.

These mineralogical analyses were performed to provide information about the potential occurrence of eutrophication processes in the pond and to check for the presence of calcite in sediment samples. Sediment samples were selected depending on ^{87}Sr/^{86}Sr ratios and calcium concentrations previously measured to cover their range of variation.

2.5. Source discrimination

Cluster analyses were performed to test the similarity or differences between sediment samples and classify them into individual categories. A hierarchical cluster analysis (HCA) combined with geochemical observations was used to discriminate between sediment samples according to the lithologies of the delineated carbonate and non-carbonate subcatchments (Fig. 1). Cluster analyses were performed with XLstat using the Ward-algorithmic method and the distance between two clusters was defined as the Euclidean distance.

A non-parametric test was used to examine similarities and differences between sediment samples. The Mann-Whitney *U* test was used to determine the ability of ^{87}Sr/^{86}Sr ratios and strontium concentrations to provide a significant discrimination between pond sediment samples at a significance level of $p < 0.05$ (Laceby et al., 2015a; Walling, 2005).

2.6. Distribution modeling

A distribution mixing model was used to quantify the relative contributions of sources to sediment (Caitcheon et al., 2012; Foucher et al., 2015; Laceby and Olley, 2014). For ^{137}Cs, a binary mixing model incorporating distributions was used:

$$Ax + B(1-x) = C \tag{2}$$

where A and B are the modeled distributions of ^{137}Cs in surface and subsurface sources respectively, C is the ^{137}Cs distribution in sediment and x is the relative contribution of the surface sources (A). x is modeled as a truncated normal distribution ($0 \leq x \leq 1$) with a mixture mean (μ_m) and a standard deviation (σ_m).

As stable isotopes do not mix linearly and are dependent of their elemental concentrations (Laceby et al., 2015b; Phillips and Koch, 2002), a different equation was used to model source concentrations ^{87}Sr/^{86}Sr ratio to incorporate their concentration dependency:

$$MMD = ABS\left(\left(E_r - \left(\sum_{s=1}^{m} E_s x_s\right)\right)/E_r\right) + ABS\left(\left(R_r - \left(\left(\sum_{s=1}^{m} C_s R_s x_s\right)/\left(\sum_{s=1}^{m} C_s R_s\right)\right)\right)/R_r\right) \tag{3}$$

where E_r is the elemental strontium concentration in the suspended sediment, E_s is the elemental strontium concentration in source (s), R_r is the strontium isotopic ratio in the suspended sediment, R_s is the strontium isotopic ratio in sources (s), x_s is the modelled proportional contribution of sources (s); and MMD is the mixing model difference. Absolute values (ABS) are summed in Eq. (3).

Non-negative constraints were imposed and normal distributions were modeled for all distributions. Pond and core sediment samples were individually modeled with their analytical error substituted as a standard deviation to model a normal distribution around each of the individual sediment samples (Evrard et al., 2016; Wilkinson et al., 2015).

Source contributions were determined with the Optquest algorithm in Oracle's Crystal Ball Software (see Laceby and Olley, 2014). To determine one optimal source contribution, the μ_m and σ_m for each source's contribution distribution (x *or* x_s) were randomly varied during the equation solving process while minimizing the median difference between both sides of Eq. (2) and the MMD in Eq. (3), and simultaneously solving these equations 2500 times with 2500 random samples (Latin Hypercube - 500 bins) drawn from each sediment and source distribution. This model simulation and solving process was then repeated 2500 times. The median proportional source contribution (x or x_s) from these 2500 additional simulations is reported as the contribution from each source.

Model uncertainty was determined by summing the modeled standard deviation (σ_m), the median absolute deviation (MAD) of the modeled source contribution and the MAD of the modeled standard deviation for the 2500 model simulations (Laceby et al., 2015a). Results (concentrations and contributions) are presented using the notation ± to express the standard error associated to one sample whereas the mean (μ) and standard deviation (σ) are used for groups of samples.

3. Results

3.1. ^{137}Cs concentrations in source and sediment samples

^{137}Cs activities in channel bank samples ranged from 0.0 to 3.0 Bq kg^{-1} (μ 1.4 Bq kg^{-1}, σ 1 Bq kg^{-1}). In surface soil samples, activities varied between 1.0 and 8.0 Bq kg^{-1} (μ 3.3 Bq kg^{-1}, σ 1.4 Bq kg^{-1}). Surface and subsurface sources were statistically different ($p < 0.0001$). Sediment had higher ^{137}Cs concentrations than their potential source samples with activities varying between 1.2 and 23.1 Bq kg^{-1} (μ 12.6 Bq kg^{-1}, σ 5.5 Bq kg^{-1}) for pond surface sediment and between 10.9 and 16.3 Bq kg^{-1} (μ 13 Bq kg^{-1}, σ 2.4 Bq kg^{-1}) for core sediment. ^{137}Cs concentrations were only considered in sediment from the top layers of the core, between 0 and 16 cm of depth ($n = 5$), to avoid disturbances from the input of ^{137}Cs from the Chernobyl accident which had peak activities at 29 cm (Foucher et al., 2015) and Fukushima ^{137}Cs fallout inputs were shown to be negligible in France (Evrard et al., 2012).

As pond and core sediment sample concentrations did not plot between the source concentrations, a Th-based particle-size correction was applied (Fig. 2a). After the Th particle size correction, activities in channel bank samples ranged between 0.0 and 1.7 Bq kg^{-1} (μ 1.2 Bq kg^{-1}, σ 0.5 Bq kg^{-1}), between 0.3 and 15.7 Bq kg^{-1} in surface samples (μ 3.8 Bq kg^{-1}, σ 3.0 Bq kg^{-1}), between 0.7 and 4.1 Bq kg^{-1} in pond sediment samples (μ 3.2 Bq kg^{-1}, σ 0.5 Bq kg^{-1}) and between 3.1 and 3.4 Bq kg^{-1} in the upper core sediment samples (μ 3.3 Bq kg^{-1}, σ 0.1 Bq kg^{-1}). The corrected sediment ^{137}Cs concentrations remained

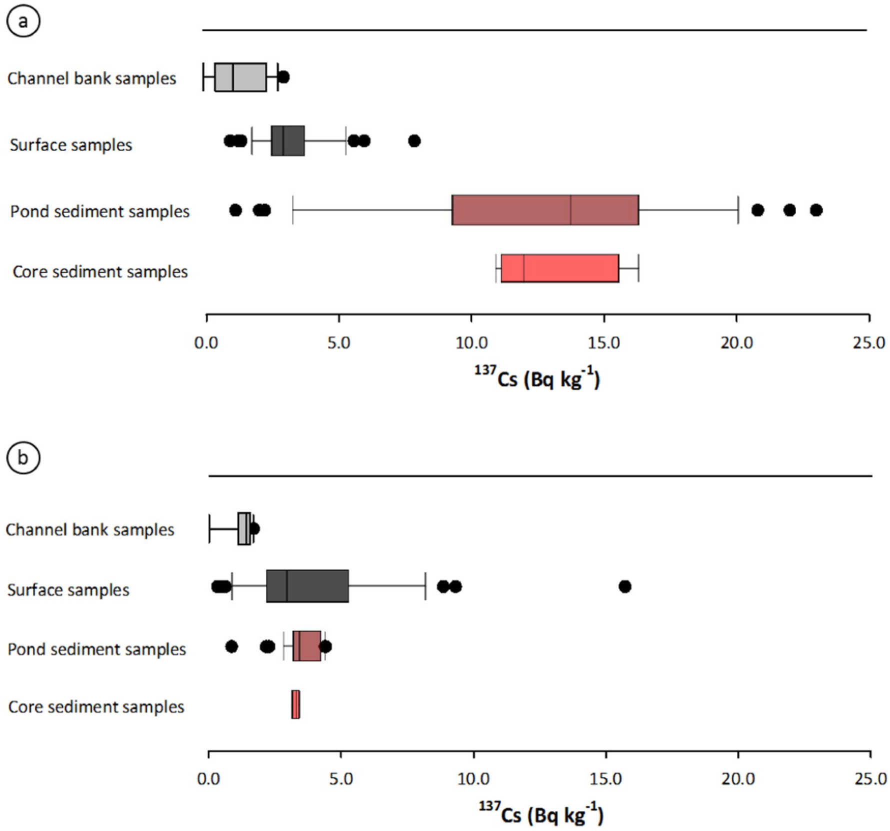

Fig. 2. ^{137}Cs activities (Bq kg^{-1}) in channel bank, soil, pond and core sediment samples before (a) and after (b) the Th particle size correction (bold horizontal line = median, box extent = 25th percentiles, error bars = non-outlier range, black dots = outliers).

within the range of corrected concentrations found in their potential sources (Fig. 2b).

3.2. Geochemical discrimination of potential sediment sources

There were large variations in sediment ^{87}Sr/^{86}Sr ratios, ranging from 0.710739 to 0.716864 (Table S2) indicating contributions from different lithological sources. The highest values (0.713867 to 0.716761, n = 8) were generally observed at the inlet of the stream draining the non-carbonate subcatchment. In contrast, the lowest values (0.711595 to 0.712502, n = 6) were found at the inlet of the stream draining the carbonate subcatchment, except for one sample (0.711999) located at the inlet of the non-carbonate subcatchment (Fig. 3a). Intermediate ^{87}Sr/^{86}Sr ratios with values between these two end-members (ranging from 0.712151 to 0.714711) characterized sediment collected in downstream sections of the pond (Fig. 3a).

A hierarchical cluster analysis (HCA) based on ^{87}Sr/^{86}Sr ratios and strontium concentrations was performed to examine potential sources of pond sediment (Fig. S2). Three main groups or clusters were discriminated based on this analysis.

Samples from Cluster 1 (N°24, 25, 26, 28, 29, 17 and 57) are located at the inlet of southern tributaries in the pond with the exception of two samples (N°17 and 57) located at the inlet of the northern tributaries and in the downstream part of the pond. These sediment samples displayed the lowest pond sediment signatures with ^{87}Sr/^{86}Sr ratios ranging between 0.711595 and 0.712316.

Samples from Cluster 2 (N°01, 07, 09, 10, 12, 13, 14, 18, 47, 49 and 61) had the highest ^{87}Sr/^{86}Sr ratios, with values varying between 0.712466 and 0.716761. They are mainly located in the inlet of the northern tributaries, with the exception of three samples (N°47, 49 and 61) located in downstream areas of the pond.

Cluster 3 (N°19, 20, 21, 22, 27, 33, 34, 38, 41, 43, 52, 70 and 73) is composed of samples located close to the inlet of the northern tributaries, in the middle and in the downstream areas of the pond. One sample (27) located in the inlet of the southern tributaries is likely an outlier. These sediment samples displayed ^{87}Sr/^{86}Sr ratios comprised between 0.712502 and 0.713467 and show intermediate values compared to those grouped in Clusters 1 and 3.

When taking into account the location of the sediment samples in the pond, the ^{87}Sr/^{86}Sr signatures and the lithologies drained by northern and southern tributaries, sediment samples from Cluster 1 can be defined as a southern/carbonate source (except 17 and 57 samples) whereas sediment samples from Cluster 2 can be referred to as a northern/non-carbonate source (except 47, 49 and 61 samples). The remaining sediment samples (from Cluster 3 and those classified in Clusters 1 and 2 but located in the downstream section of the pond) were hypothesized to be derived from a mixture of sediment originating from the two previously defined end-members. Scatter plots with ^{87}Sr/^{86}Sr and elemental ratios (Rb/Sr, Ca/Sr, Mg/Sr, K/Sr, Na/Sr) were also used to confirm the discrimination between these sediment sources (Fig. S3). Therefore, sediment samples collected in the two inlets draining the carbonate and non-carbonate subcatchments were used to characterize the two main potential sources of downstream pond sediment.

In addition to these two main sources, ^{87}Sr/^{86}Sr ratios were measured in carbonate rocks, shelly sands and fertilizers. In the carbonate rocks, signatures varied between 0.707968 and 0.708789 while the shelly sand signature reached a value of 0.709538. In fertilizers typically used in this catchment, strontium isotopic ratios varied between 0.707877 and 0.716224. The N fertilizer had the highest value (0.716224). However, it was removed from further analysis owing to a very low Sr concentration (0.5 mg kg^{-1}). In P.K and N.P.K fertilizers, Sr ratios varied between 0.707877 and 0.709178 (Table S6). In addition,

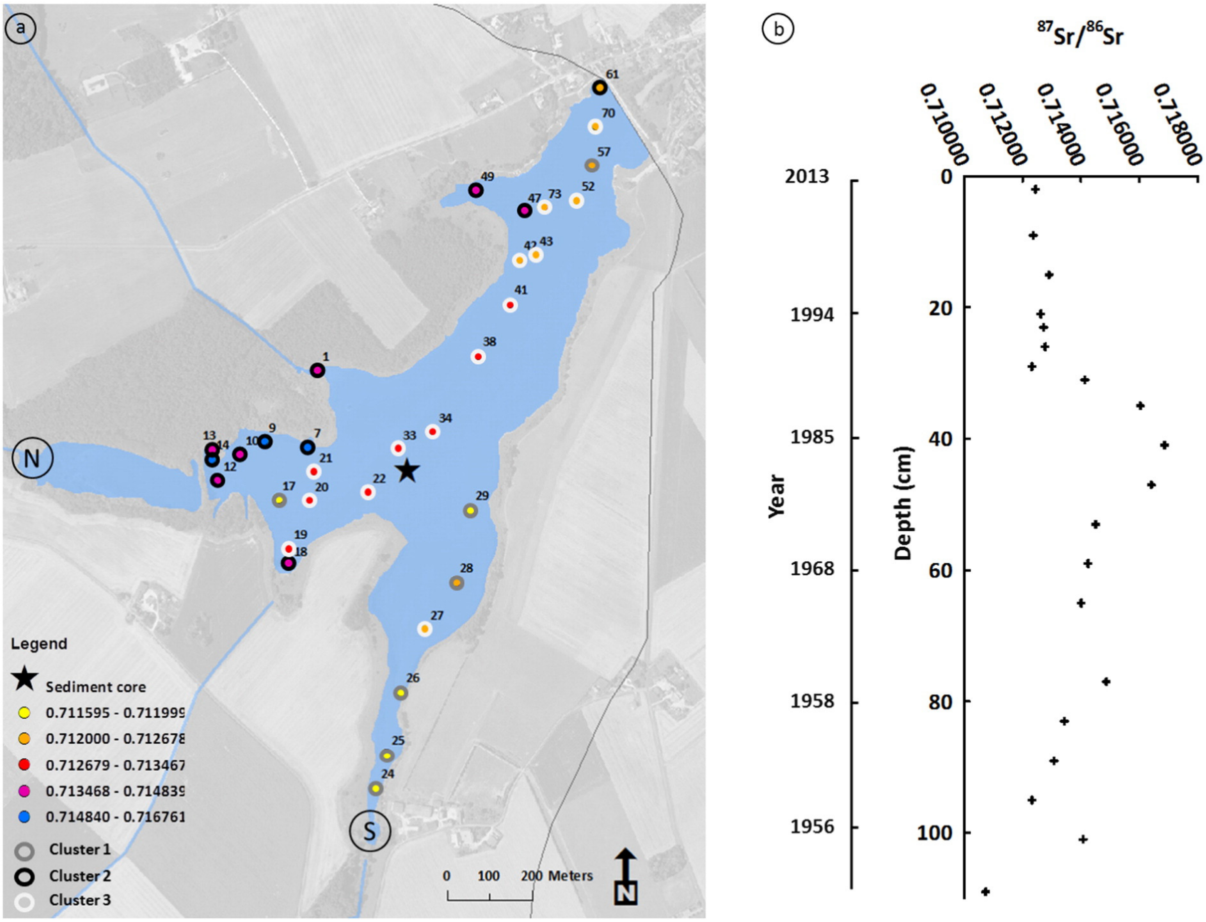

Fig. 3. Spatial (a) and temporal (b) variations of $^{87}Sr/^{86}Sr$ ratios in pond and core sediment samples. N and S correspond to the northern and southern inlets of the main tributaries, respectively (a).

elevated zinc concentrations were measured in these samples (136 and 184 mg kg^{-1}, respectively, see Table S6). High zinc concentrations were also observed in surface pond (with concentrations ranging between 67 and 124 mg kg^{-1}) and core sediment (Table S3 and Table S4). In the core, a progressive increase in zinc concentrations was observed from the bottom (47 mg kg^{-1}) to the top (102 mg kg^{-1}).

3.3. Temporal variations of $^{87}Sr/^{86}Sr$ ratios in core sediment samples

In the Louroux sediment core, $^{87}Sr/^{86}Sr$ ratios ranged from 0.710739 to 0.716864 (Fig. 3b). The lowest $^{87}Sr/^{86}Sr$ ratio (0.710739) was observed in 1955, on the bottom of the core. From 1956 to 1976, $^{87}Sr/^{86}Sr$ ratios tended to increase to a maximum of 0.716864. Then, from 1976 to 1986, $^{87}Sr/^{86}Sr$ ratios decreased until they stabilized with values ranging between 0.712318 and 0.712900 from 1986 to 2013 (Fig 3b). Strontium isotopic signatures in core sediment samples have the same range of variations as those observed in pond sediment samples.

3.4. Mineralogical characterization and selective extraction performed on selected core and pond sediment samples

XRD analyses indicated the presence of calcite in all core sediment samples, with contributions varying between 10 and 32% (Table S1). SEM micrographs confirmed the presence of calcite in the sediment samples. The calcite was well precipitated, partially precipitated and potentially associated with clays depending on the samples (Fig. S4f, Fig S4a-b-c-d-g-h and Fig. S4a-b-c-d-i, respectively). Furthermore, silica tubes and diatoms were observed in two core sediment samples (Fig. S4e and g, respectively).

Between 1955 and 1963, the proportion of strontium contained in the exchangeable and carbonate fraction (F1) oscillated between 56 and 73%, the lowest proportion being observed on the bottom of the core. The lowest F1 fraction of the entire sequence (43%) was observed in 1976, before increasing to reach a stable state between 1986 and 2005 with a F1 fraction ranging between 68 and 73% (Fig. 4a).

Between 1955 and 2005, the proportion of calcium contained in the F1 fraction increased from 62% to a maximum of 90%. The highest contributions were observed between 1976 and 2005 (Fig. 4b). $^{87}Sr/^{86}Sr$ ratios measured in the F1 fraction increased from 1955 to 2005, following the same trends as calcium in this fraction (Fig. 4). The two lowest $^{87}Sr/^{86}Sr$ ratios (0.709216 and 0.709236) were observed in 1955 and 1957. A strong increase was observed from 1957 to 1976, and stable ratios (0.709380 to 0.709395) occurred between 1986 and 2005, when the stabilization of the F1 fraction was observed.

$^{87}Sr/^{86}Sr$ ratios plotted between the signatures of the carbonate rocks, the fertilizers and the shelly sand, suggesting a potential impact of all these sources on the isotopic signature of the core sediment samples (Fig. 5). Sediment sources were thus modeled following a tributary tracing approach (Laceby et al., 2015a; Vale et al., 2016). With this approach, pond sediment samples from inlets of the two main tributaries were modeled as the two main lithological sources (carbonate and non-carbonate) to downstream pond sediment and the sediment core. The potential influence of carbonate rocks, shelly sands, fertilizers, and eutrophication is incorporated within these two tributary sources with this sediment-based sampling approach for surface pond sediment.

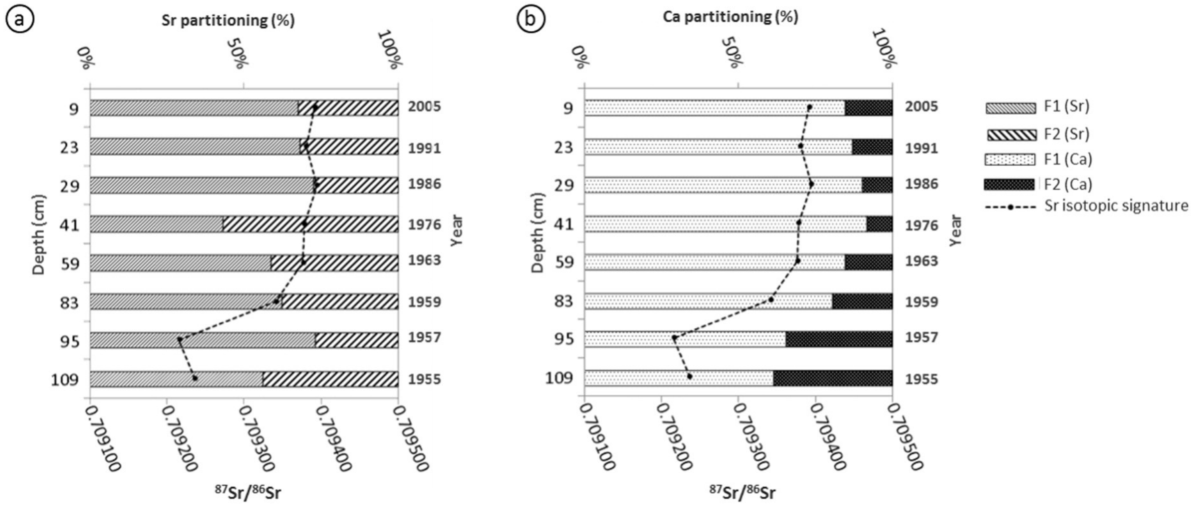

Fig. 4. Strontium (a) and calcium (b) partitioning in core sediment between two defined fractions F1 (exchangeable and carbonate fraction) and F2 (residual fraction) and $^{87}Sr/^{86}Sr$ ratios measured in the fraction F1.

3.5. Modeling results

3.5.1. Spatial variations of sediment sources in the pond

Surface sources dominated the supply of sediment to the pond (μ 82%, σ 1%). Surface source contributions varied between 26 ± 1% and 100 ± 4%, and fifteen sediment samples were modeled to be derived exclusively from surface sources (Fig. 6a). Samples characterized by a significant contribution from subsurface sources were mainly located at the inlet of the two main tributaries (the Beaulieu and Grand Bray streams, with contributions of the channel banks varying between 12 ± 1% and 67 ± 1%) or near pond banks in the downstream section of the pond with contributions varying between 7 ± 2% and 75 ± 1%.

Mixing model results using pond sediment samples from the inlet of the two main tributaries as subcatchment sources indicated that the carbonate tributary supplied between 4 ± 1% and 100 ± 1% of downstream sediment in the pond (μ 48, σ 1%) (Fig. 6b). One sediment sample (N°17) located in the inlet of the non-carbonate tributary had a high carbonate contribution of 89 ± 1%. In the central part of the pond, sources contributions were well balanced with the carbonate tributary inputs ranging between 52 ± 1% and 56 ± 1%. In the downstream area of the pond, the carbonate tributary contributions were more variable, with the lowest and the highest contributions observed in this well-mixed section.

3.5.2. Temporal variation of sediment sources in the core

Modeling results indicate that during the last 17 years, surface sources supplied the majority of core sediment, with a mean contribution of 89 ± 3% (Fig. 7b). Overall, contributions varied between 80 ± 3% and 96 ± 5%. Between 1999 and 2001, a slight increase in the surface source contribution was observed with values increasing from 86 ± 1% to 96 ± 5% before decreasing again between 2009 and 2013 to values between 80 ± 3% and 83 ± 1%. As previously indicated, ^{137}Cs concentrations were only considered in the top 0-16 cm to avoid disturbances from the input of ^{137}Cs from the Chernobyl accident recorded at 29 cm (Foucher et al., 2015). Accordingly, contributions were not estimated below a depth of 16 cm.

Between 1955 and 1957, high variations in sediment spatial sources were observed (Fig. 7a). In 1955, sediment exclusively originated from the southern/carbonate tributary (100 ± 1%). Then, dramatic changes were observed with a dominant contribution from the northern/non-carbonate tributary (96 ± 4%) in 1956. The main source changed again, with the dominance of the southern/carbonate tributary (89 ± 2%) in 1957. From 1957 to 1981, the contribution of the northern/non-carbonate tributary progressively increased to a maximum contribution of 100 ± 13%. Then, between 1981 and 1986, these contributions decreased to reach a stable state in the upper part of the core (0–31 cm of depth) where the northern/non-carbonate tributary contributed between 30 ± 1% and 47 ± 1% of sediment from 1986 to 2013.

4. Discussion

4.1. Surface and channel bank source contributions

Surface soils were identified as the main source of surface pond sediment. This result is consistent with the observations of Foucher et al. (2015) for suspended sediment collected during flood events upstream of the Louroux pond. They showed that virtually all the sediment originated from the soil surface (μ 98%, σ 2%). However, during low flow periods, they found that suspended sediment transiting the river network had elevated subsurface source contributions (μ 60%, σ 2%) (Foucher et al., 2015). In this current research, subsurface contributions to pond sediment were shown to be significant in areas located in the inlets of the main tributaries close to the pond banks (with contributions ranging between 12 ± 1% and 67 ± 1%). In the rest of the pond, surface sources dominated (μ 86%, σ 1%). The potential erosion of the banks of the pond may also explain the significant contributions of the subsurface source observed near the pond banks and in the downstream

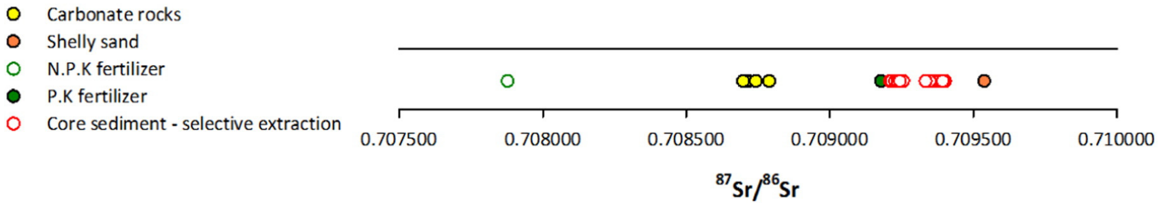

Fig. 5. $^{87}Sr/^{86}Sr$ ratios variations in carbonate rocks, shelly sand, fertilizers and the exchangeable/carbonate fraction of core sediment samples.

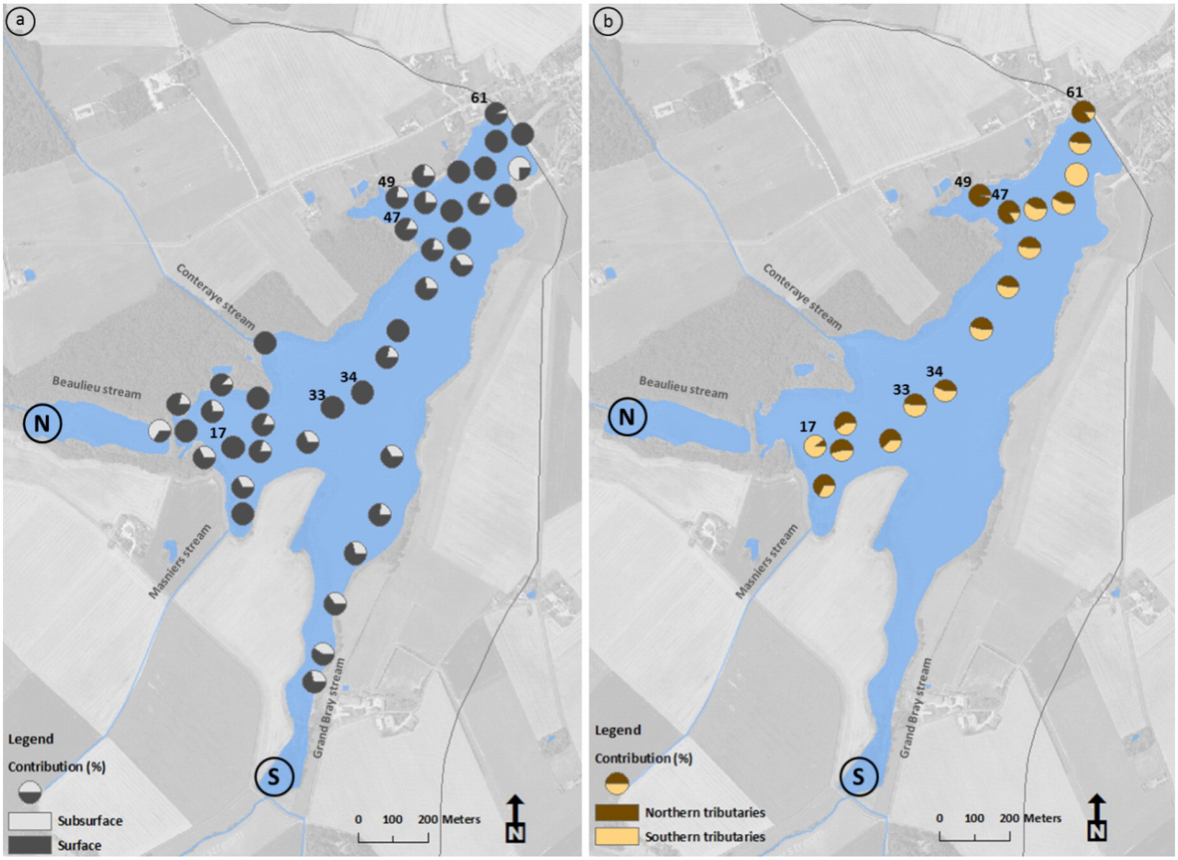

Fig. 6. Contribution of the surface and subsurface sources (a) and of the carbonate (southern) and non-carbonate (northern) sources (b) to the surface sediment collected in the Louroux pond. N and S correspond to the northern and southern inlets of the main tributaries.

section of the pond, simply owing to their proximity, or possibly smaller tributaries draining into these locations (e.g. N°47, 49).

In the sediment core, there were also subsurface contributions (maximum contribution of 20 ± 3%). These contributions remained stable (μ 11%, σ 3%), indicative of an ongoing channel bank sediment source contribution, though less than what Foucher et al. (2015) modeled for the low-flow conditions in 2013. Overall, channel bank contributions to the pond and core sediment were similar (μ 18%, σ 1% and μ 11%, σ 3% respectively). In fact, the core sediment mean subsoil contribution between 2009 and 2013 (18%) was equivalent to the mean subsoil contribution for the pond sediment. These results suggest that although surface sources dominated sediment supply to the pond during the last seventeen years, channel bank contributions should not be neglected.

4.2. Tributary contributions to pond sediment

Modeling results based on ^{87}Sr/^{86}Sr ratios indicate that the southern/carbonate and northern/non-carbonate tributary contributions to pond sediment were nearly equivalent (μ 48%, σ 1% and μ 52%, σ 3% respectively). Over the last seventeen years, both tributaries contributed in stable proportions to sediment sampled in the core (μ 64%, σ 1% for the southern/carbonate tributary).

The southern tributaries drain most of the carbonate substrates that only cover 24% of the catchment surface area and their derived sediment were modeled to contribute more than half of the downstream pond sediment. Therefore, this research implies that the southern/carbonate area supplied disproportionately more sediment to the pond than the northern/non-carbonate area.

One sediment sample (N°17) located in the inlet of the non-carbonate tributary was shown to mainly originate from the carbonate area (89 ± 1%). Field observations indicated that crushed limestone was used to stabilize channel banks in that section of the pond and a mix of sediment and this limestone may have been sampled at that location. Three sediment samples (N°47, 49 and 61) located in the downstream section of the pond were statistically classified as northern/non-carbonate (Cluster 3). Field observations revealed that ephemeral tributaries draining flint clay substrate areas flow into the pond at these locations, which may explain their classification as northern/non-carbonate sediment.

Model results obtained from the core samples demonstrate high variations in lithological sources from 1955 to 2013. The variations are likely related to the spatial evolution of the land consolidation and river design schemes implemented in the catchment since the 1950s. The drastic changes in source contributions observed between 1955 and 1957 could be interpreted as the response to a large-scale phase of land consolidation in 1955 (Foucher et al., 2014). The increasing contribution of the northern/non-carbonate tributary from 1957 to 1981 may be directly related to the implementation of a dense drainage network, the creation of ditches, and the removal of hedges in this northern/non-carbonate area. From 1981 until 1986, the contribution of the carbonate tributary increased and then reached a relatively steady state between 1986 and 2013, with carbonate tributary contributions fluctuating between 53 ± 1% and 70 ± 1%. The Beaulieu pond, located directly upstream of the Louroux pond and currently almost filled with sediment, could act as a buffer, reducing the sediment contributions from the northern/non-carbonate tributary to downstream Louroux pond sediment.

^{87}Sr/^{86}Sr ratios, calcium and strontium concentrations (Table S5) were measured in the exchangeable and carbonate fraction of a selection of core sediment samples to provide information on the biological and chemical processes that may have occurred in the

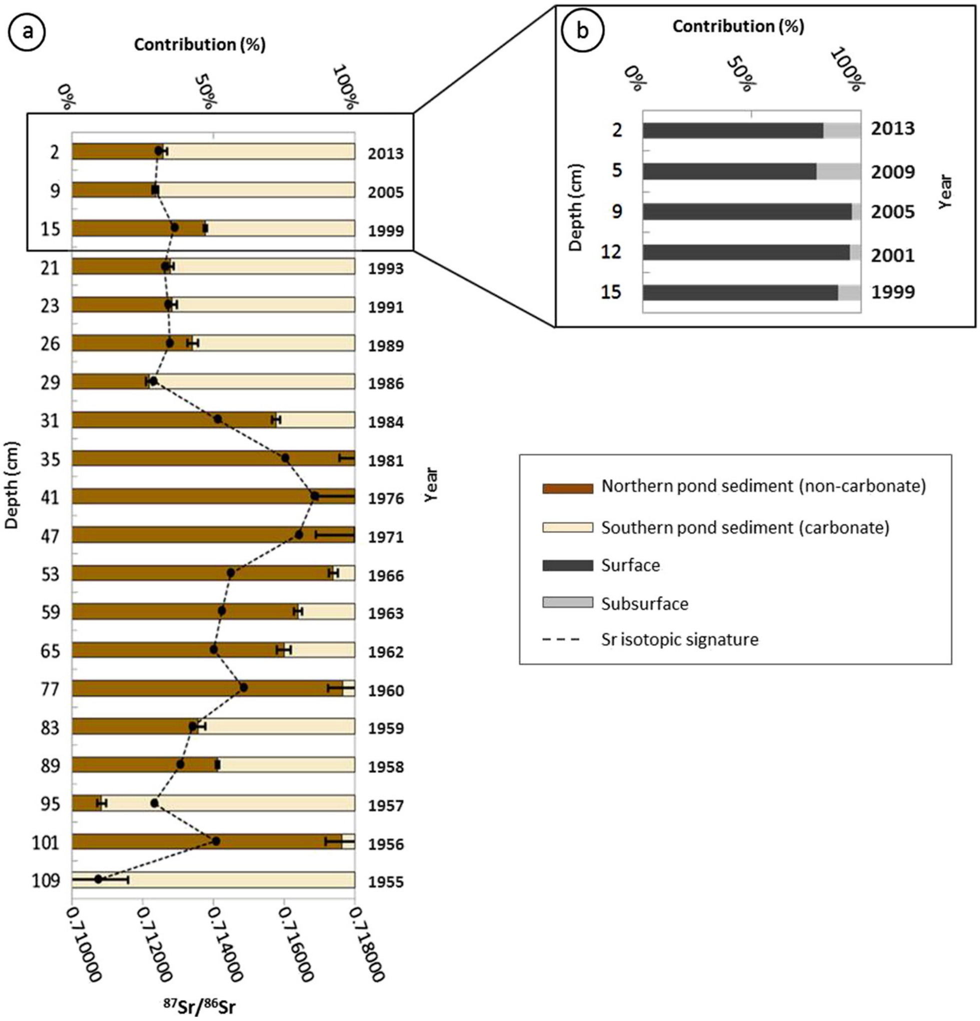

Fig. 7. Evolution of the lithological (a), surface and subsurface (b) sediment sources contributions and $^{87}Sr/^{86}Sr$ ratios along the sediment core (error bars reflect the modelling standard deviation for each sediment sample).

Louroux pond. Results indicated that the carbonate fraction (F1) in the core sediment increased between 1955 and 2005 and had a maximal contribution since 1976. This may be related to higher amounts of carbonates precipitated in the pond during this period, which confirms previous findings showing the occurrence of a progressive eutrophication of the pond. This is confirmed by the presence of algae typical of eutrophic environments and the increase of autochthonous material, with contributions estimated between 44 and 50% (Foucher et al., 2014). These observations are also consistent with the results of XRD and SEM analyses.

Well crystallized calcite was exclusively observed on the bottom of the core (Fig. S4f) during a period that occurred before the implementation of land consolidation programs in the catchment. In contrast, partially precipitated calcite, which is potentially easier to extract, was observed on top of the core, suggesting the occurrence of in situ precipitation. Previous studies conducted in the Loire River (France) observed authigenic calcite precipitation during low flow in summer (Négrel and Grosbois, 1999). In addition, it has been demonstrated that under temperate climates, calcite precipitation can be directly related to inputs of nutrients and thus to primary production (Hamilton et al., 2009). Strontium contributions in the F1 fraction did not follow exactly the same trend as calcium contributions, with a slight shift towards higher ratios in the most recent sediment. This suggests that strontium sources of the carbonate fraction evolved through time and did not exclusively originate from lithological carbonates. Additional sources, such as fertilizers, may potentially explain strontium variations in the carbonate fraction.

4.3. Implications for sediment tracing, catchment management and future studies

The tributary tracing approach may be a useful approach to addressing potential eutrophication, anthropogenic inputs (fertilizers) and in situ precipitation when using $^{87}Sr/^{86}Sr$ ratios for tracing sediment in agricultural catchments. In particular, fertilizers are known to be a major source of contaminants (Zn, Cu, Cd, Pb and Ni) in agricultural soils (Nziguheba and Smolders, 2008) and erosion of these contaminated soils may lead to the deterioration and eutrophication of water bodies (Otero et al., 2005; Vitoria et al., 2004). Furthermore, strontium concentrations may vary between 10 and 4500 mg kg^{-1} in phosphate fertilizers (Otero et al., 2005). Although $^{87}Sr/^{86}Sr$ fractionation in ecological systems is negligible, the redistribution and accumulation of strontium originating from fertilizers in soils may contribute to changes in their isotopic signatures (Borg and Banner, 1996). As an example, Hosono et al. (2007) indicated that 25% of the dissolved Sr was derived from fertilizers in rivers draining a Japanese agricultural catchment. In the Louroux catchment, P.K and N.P.K fertilizers were characterized by high zinc concentrations. Similarly, high Zn concentrations were measured in surface pond sediment and in core sediment since 1983. $^{87}Sr/^{86}Sr$ ratios measured in the mobile fraction (F1) of core sediment were between the signatures of carbonate rocks and shelly sands and the signature of the P.K fertilizers. These results suggest that fertilizers have impacted sediment composition in this catchment since the beginning of the 1980s.

The potential impact of these fertilizers on sediment and source soil properties resulted in the need to adopt a tributary tracing approach in this current research. This approach directly incorporates fertilizers and other potential influences on $^{87}Sr/^{86}Sr$ ratios when tracing the source of downstream sediment in the Louroux Pond. Although the sediment core $^{87}Sr/^{86}Sr$ ratios plotted within the tributary source range, it would be useful for future research to compare 3–5 sediment cores of equivalent length, sampled in each tributary, to sediment cores downstream in order to comprehensively investigate tributary $^{87}Sr/^{86}Sr$ source ratios and variations over an equivalent temporal period.

Importantly, these results demonstrate the need to better manage cultivated soils. Land consolidation schemes, modifications in farming practices and in catchment management were shown to have a strong impact on spatial variations of the main sources of sediment. To date, sedimentary archives were mainly collected in lacustrine environments to reconstruct historical sediment fluxes related to environmental changes over longer periods (typically the Holocene period). However, they were mostly collected in mountainous environments (Arnaud et al., 2012; Chapron et al., 2002; Simonneau et al., 2013). Sediment cores were also used to reconstruct concentrations of various contaminants in sediment with time in a large number of rivers of the world (Barra et al., 2001; Bertrand et al., 2013; Elbaz-Poulichet et al., 2011; Rawn et al., 2001). This current approach, combining radionuclide and isotopic geochemical measurements to pond sediment cores, provides important information on sediment source evolution in agricultural lowland catchments in relation to changes in land use and agricultural practices.

5. Conclusions

A targeted fingerprinting approach that combined fallout radionuclides (^{137}Cs), including a thorium-based particle size correction, and strontium isotopic geochemistry ($^{87}Sr/^{86}Sr$) was used to examine spatial and temporal variations of sediment sources in a lowland, drained agricultural catchment. A within-pond tributary tracing approach was developed to mitigate the potential influence of eutrophication, anthropogenic inputs (fertilizers) and in situ precipitation. This research demonstrated the utility of coupling radionuclides and strontium isotopic geochemistry to quantify sediment sources and collecting sediment in pond tributary inlets to use as a source surrogate to trace the origin of sediment sampled downstream.

Surface sources dominated the Louroux pond sediment supply (μ 82%, σ 1%). The tributaries draining both the carbonate and the non-carbonate subcatchments contributed approximately half of the surface pond sediment. In contrast, large fluctuations of these tributary contributions were modeled from the analysis of a sediment core. These variations likely reflect the spatial pattern of the land consolidation scheme implemented in this catchment that started in the 1950s.

This research demonstrates the utility of using sediment archives to reconstruct the impact of large scale catchment modifications on sediment dynamics. Further analysis of sediment draining agricultural areas should be encouraged to improve our understanding of erosion processes that occurred in these environments. Understanding past impacts of land management on soil erosion and sediment dynamics is fundamental to improving future best management practices in agricultural catchments.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.05.093.

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