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► **To cite this version:**

Frédérique Eyrolle, Amandine Morereau, Mathilde Zebracki, Valérie Nicoulaud Gouin, Hugo Lepage, et al.. Anthropogenic legacy of potassium-40 in French large rivers reconstructed from sediment cores. *Science of the Total Environment*, 2024, 954, pp.176479. 10.1016/j.scitotenv.2024.176479 . hal-04764619

HAL Id: hal-04764619

<https://hal.science/hal-04764619v1>

Submitted on 4 Nov 2024

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Anthropogenic legacy of potassium-40 in French large rivers reconstructed from sediment cores

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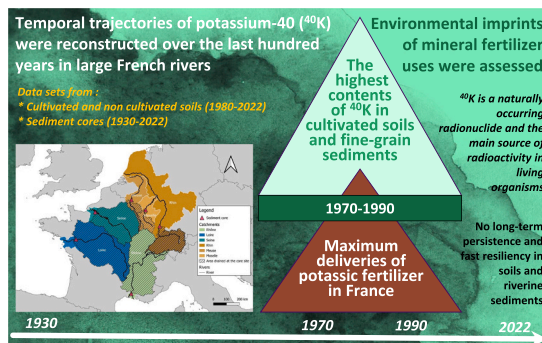
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HIGHLIGHTS

- Potassium-40 contents were measured in sedimentary archives of large French rivers.
- The reconstructed trajectories covered almost the last century in most cases.
- The highest contents in fine-grain sediments were observed over the 1970–1990 period.
- This period coincided with the maximum potassic fertilizer delivery in France.
- Since the 1990s, contents converged towards referential values for most of the rivers.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Bo Gao

ABSTRACT

Environmental imprint of inorganic fertilizer uses was assessed over the last hundred years at the downstream part of large French rivers (Loire, Moselle, Rhine, Rhone, Meuse and Seine rivers) based on Potassium-40 (⁴⁰K) activity concentration data sets acquired from soil monitoring (1980–2022) and from sediment cores collected from 2020 to 2022 to reconstruct the temporal trajectories of ⁴⁰K activity concentrations since the beginning of the last century. Cultivated soils were significantly enriched in ⁴⁰K compared to non-cultivated ones in the 1980s and 1990s when they turned back to the contents of non-cultivated soils during the following decades. In riverine sediments, all the rivers displayed close ⁴⁰K temporal trajectories with peaking ⁴⁰K contents in fine grain size

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<https://doi.org/10.1016/j.scitotenv.2024.176479>

Received 22 July 2024; Received in revised form 6 September 2024; Accepted 21 September 2024

Available online 24 September 2024

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sediments in the 1980s. Maximum ^{40}K enrichment factors from this period were related to the proportion of agricultural areas in the river catchment. In the Loire and Moselle rivers, some high ^{40}K contents were associated with sandy sedimentary strata deposited by flood events before the end of the 1950s due to the presence of potassium enriched minerals. The comparison of ^{40}K activity concentration in sediments with potassic fertilizer delivery in France highlighted very similar temporal trajectories giving evidence that the uses of potassic fertilizers imprint the riverine sediments of most French large rivers. Finally, the environmental resilience face to this anthropic pressure was fast as ^{40}K levels decreased immediately after the decreases of the delivery in most of cases.

1. Introduction

The naturally occurring long-lived Potassium-40 (^{40}K) is considered as one of the most abundant radionuclides of telluric origin together with the products of the decay chains of uranium-238 (^{238}U), uranium-235 (^{235}U) and thorium-232 (^{232}Th). Present on Earth since its formation, it persists even today due to its very long radioactive half-life of $1.25 \cdot 10^9$ years and contributes to the natural radiation to which humans are exposed both from the internal exposure originating from radionuclides in diet and from inhaled radon gas, and from the external exposure generated by cosmic rays and γ -rays emitted by radioactive elements in soils, rocks and building materials. Because potassium is an essential element for life, ^{40}K constitutes the main source of radioactivity in living organisms, greater than that constituted by carbon 14 even though there are 1.2 radioactive atoms of ^{40}K for every 10,000 nonradioactive atoms of potassium. A 70 kg man would undergo the disintegration of 4400 atoms of ^{40}K every second, or approximately 0.39 mSv/year per ^{40}K compared to 0.01 mSv/year attributable to ^{14}C . Potassium is part of the composition of many minerals naturally present in soils (potassium feldspars, micas) and rock weathering is therefore a significant source of potassium, particularly in unfertilized ecosystems, such as forest systems. Unlike phosphorus, potassium is not present in soil organic matter and in cultivated systems, the supply of potassium through mineral weathering is much lower than potassium exports through crops. This is the reason why potash fertilizers are generally applied to crops, in the form of simple fertilizers, or mixed with other fertilizers namely phosphate fertilizers of different combination and by-products such as phosphor-gypsum. Potash fertilizers are extracted from a variety of geological potassium salt deposits around the world. The salts are processed to remove impurities and converted into a variety of inorganic fertilizers which are translocated onto agricultural areas. Almost all the world's phosphate fertilizers are derived from phosphate rocks.

Inorganic fertilizers contain a wide range of trace contaminants including trace metals, among them cadmium, lead arsenic chromium and zinc, with greatly varying contents, and phosphate fertilizers would be the most enriched ones (Alloway, 1990; Al-Attar et al., 2012; Thomas et al., 2012; Raven et al., 1998; Khan et al., 2018). Several studies have been conducted to evaluate the effect of fertilizers on trace metal accumulation in soils (e.g. Loganathan et al., 1995; Chen et al., 2007; Luo et al., 2009; Czarnecki and Düring, 2015; Kleeberg et al., 2016). Phosphate fertilizers not only contain trace metals, but also naturally occurring radioactive materials, such as the radionuclides ^{238}U , ^{232}Th , ^{210}Po , ^{226}Ra and few amounts of ^{40}K (Mustonen, 1985; FAO, 2009; Sönmez et al., 2007; Kara et al., 2004; Hassan et al., 2016) because the major constituent of phosphate rock is the P_2O_5 -enriched mineral apatite in which radionuclides may be incorporated through ionic substitution or by adsorption (Khan et al., 2018). The radionuclide contents in fertilizers varies greatly depending on the originating rock and several studies were dedicated to the availability of radionuclides in the fertilizers and their potential risk in plants, and human and animal health (e.g. UNSCEAR, 1988, 1993; Saleh et al., 2007; Becegato et al., 2008; Hassan et al., 2016). Tahir et al. (2009) studied ^{40}K activity concentration in fertilizers used in Pakistan and reported that the average value, 885 ± 220 Bq/kg, was higher than the values reported from the

USA (200 Bq/kg) and Germany (720 Bq/kg) but lower than the reported concentrations from Saudi Arabia (2818 Bq/kg) and Finland (3200 Bq/kg). Nowak (2013) reports ^{40}K contents in mineral fertilizers in Poland reaching almost 17,000 Bq/kg while Boukhenfouf and Boucenna (2011) reported that ^{40}K activity concentrations in compounds commercially named NPK (nitrogen (N), phosphorus (P) and potassium (K)) and NPKs (sulfate-based fertilizer) would lie between 14 and 31 times above the world average. According to UNSCEAR (2000), the world average value of activity concentration for ^{40}K in soil range from 140 to 850 Bq/kg (mean value 370 Bq/kg) and both categories of soil, virgin and fertilized, was within the world average range.

During the 1970s and 1980s, one-third of the increase in cereal production worldwide and half of the increase in India's grain production have been attributed to increased fertilizer consumption (FAO, 2013). In France, potash fertilizers were produced in the Alsace region between 1910 and 2002 and during almost one century, >90,500 kt of potash were extracted in the Mines de Potasse d'Alsace (MDPA). Concerning the agricultural usage, >83,300 kt of potash fertilizers were delivered in French agricultural exploitations from 1910 to 2023. In addition, phosphate fertilizers were also largely used in French agriculture and >77,300 kt were delivered in the country between 1950 and 2023. Today, both fertilizers are still used in French agriculture, but the quantities delivered are decreasing since the 1970s in the case of phosphate fertilizers and since the 1990s for potash fertilizers.

Potassium in fertilizers easily dissolves to enhance contents in agricultural soils and its uptake by crops. Potassium is held in the soils depending on their cation exchange capacity. Soils with finer particles, such as clay, and organic matter, can hold more positively charged ions than soils with larger particles, such as sand. Depending on both soil potassium saturation and nature, a part of the added amounts can transfer towards river systems due to soils leaching, weathering and erosion leading to a potential enhancement of ^{40}K activity concentration in waters and sediments. To evaluate such environmental imprints legated by inorganic fertilizer uses in agricultural catchments we compiled data sets from cultivated and non-cultivated soils collected in France in the frame of long-term monitoring programs and from sediment layers extracted from sedimentary cores collected at the downstream sections of large French rivers. The main objective of this study was to retrace the temporal trajectories of ^{40}K activity concentration in French soils and sediments over the last decades to (i) decipher the causal link between ^{40}K activity concentration in such environmental systems and inorganic fertilizer uses in the catchment, (ii) to calculate ^{40}K enrichment factor over years referring to geochemical backgrounds and (iii) to estimate environmental resiliency of river systems faced to inorganic fertilizer uses in their catchments.

2. Material and methods

2.1. Documentary archives on mineral fertilizers uses in France

Fertilizers delivery data were collected from two main documentary sources: first in the archives of the French National Institute of Statistics and Economic Studies (INSEE), for the period covering 1910 to 2001. Secondly data were extracted from historical campaign reports and from the website of the National Union of French Furniture Industries

(UNIFA), for the period between 2002 and 2018.

2.2. Location of core samplings and characteristics

Sediment cores were sampled between 2020 and 2022 in downstream sections of the Loire, Rhone, Rhine, Seine, Meuse and Moselle rùjivers in France (Fig. 1 and Table 1) by using ancient maps as well as aerial photographs, available literature and field investigations to identify zones where sediment deposition was as continuous as possible over the last several decades as described in detail in Eyrolle et al. (2024).

2.3. Sediment sampling and core dating

Apart from the Seine core, which was collected by using an Amaury coring equipment, all the sediment cores were collected by using a percussion driller (Cobra TT, SDEC, France) with transparent PVC tubes (diameter 46 mm or 100 mm) as already described in Eyrolle et al. (2024). For cores exceeding 1-m depth, a master core was obtained by sampling twice successive 1-m sediment cores across <1 m² surface area. The second coring was vertically shifted by 50 cm compared to the first one to preserve sediment from interface disruptions. Once back to the laboratory, each 1-m core was longitudinally cut and opened for stratigraphic analyses, and then laterally cut. From 1 to 16.5 cm sediment slices were successively sampled from the surface to the depth depending on the visual observation of core stratigraphy. Slices were stored at -25 °C and freeze-dried under dehydrated nitrogen flux to avoid any atmospheric exchange and sieved to 2 mm before further

Table 1

Location of the sampling sites and amount of agricultural land* coverage (in %) in the surface area drained at the coring site (numbered in decreasing order). *: Non-irrigated arable land, permanently irrigated land, Rice fields, Vineyards, Fruit trees and berry plantations, Olive groves, Pastures, Complex cultivation patterns, Land principally occupied by agriculture, with significant areas of natural vegetation, Agro-forestry areas; The cumulative areas by type of land use and by watershed were obtained using the Spatial Analyst Tool of the ArcGis 10.8 software and its function Tab area.

River	Location	Y (WGS 84)	X (WGS 84)	Land use (% agricultural)
Loire	Montjean sur Loire	47.392778	-0.856417	72
Seine	Orival	49.303667	0.997111	66
Moselle	Berg	49.430889	6.307806	53
Meuse	Givet	50.152843	4.833220	52
Rhone	Fourques	43.706861	4.613528	37
Rhin	Rhinau	48.272417	7.679583	36

analyses. Overall, almost 350 sediment samples were analyzed.

Sediment cores were dated by using both Caesium-137 (¹³⁷Cs) and other chronological tracers such as ²⁴¹Am, plutonium isotopes and flood events, and Lead-210 isotope in excess (²¹⁰Pb_{xs}) as a daughter radionuclide of the ²³⁸U radioactive decay series produced by gaseous ²²²Rn decay (Goldberg, 1963, Appleby and Oldfield, 1978; Foucher et al., 2021). These methods are widely used to date recent sediment deposits (100 last years) because ¹³⁷Cs and ²¹⁰Pb half-life (30.08 y and 22.20 y, respectively) allow to cover several decades of sediment deposition. Based on this methodological approach age versus depth models were

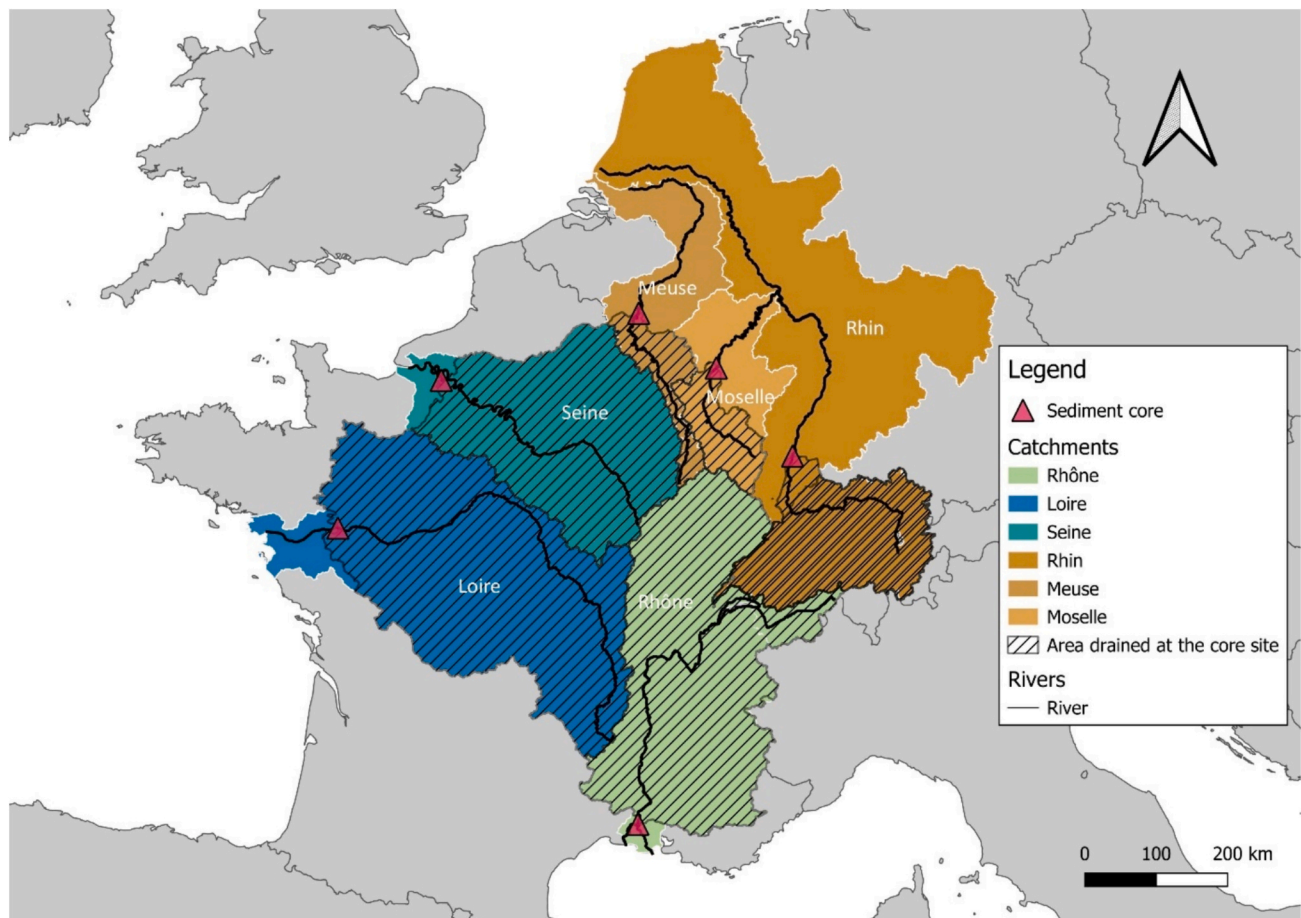


Fig. 1. Location of Loire, Rhone, Rhine, Seine, Meuse, and Moselle cores with associated drained watersheds (shaded); All the cores collected on emerged areas corresponded to sites occupied by riparian forests except the Meuse where grassland vegetation dominates. The Seine core was collected within a continuously submerged secondary channel; from Eyrolle et al. (2024).

established for each sedimentary core and the results are reported in detail in Eyrolle et al. (2024). In brief, these models allowed to attribute the mean age of each sedimentary strata samples based on the assessment of apparent sedimentation rate (ASR) values along the core profile. Sediment depth covering the last century ranged from around 80 cm for the Rhine and Meuse rivers until >400 cm for the Seine River leading to mean ASR varying from 0.8 to 4 cm/y. Apart from these mean values, specific ASR ranging from 0.3 to 11.4 cm/y were determined among the various sedimentary profiles. Uncertainties on ASR and consequently on estimated mean age of the sedimentary strata directly depend on the benchmarks deciphered along the depth profile and the thickness of the sedimentary strata where the benchmarks were identified. Uncertainty on estimated mean age mechanically increases as the ratio between ASR and the sedimentary strata thickness decreases. In most of cases, uncertainties on mean age would be <3 years by considering that ASR is constant between two successive benchmarks what cannot be strictly testified.

2.4. Low-background gamma spectrometry

Sedimentary core samples were analyzed by gamma spectrometry. Dry samples were conditioned in 17- or 60-mL tightly closed plastic boxes for gamma counting using low-background and high-resolution Germanium Hyper pure (HPGe) detectors in the Environmental Radioactivity Metrology Laboratory (IRSN/LMRE in Orsay). ^{40}K activity concentrations were measured under accreditation (COFRAC N°1-0993) (IRSN/LMRE, Orsay) by high resolution gamma-ray spectrometry following the ISO 18589-3:2023 standard (ISO 18589-3, 2023) using its characteristic peak at 1460.822 keV with 10.55 % emission intensity. The High Purity Germanium (HPGe) detectors used was low background Broad Energy Germanium detectors (BEGETM 5030, Canberra/Mirion) installed in the shielded room situated in the second basement of the laboratory under a 3 m slab of borated concrete to reduce the cosmic ray induced background. The HPGe was equipped with anti-cosmic veto (plastic scintillators) to further decrease this contribution. The shielded room made of 10 cm lead bricks internally covered by 5 mm copper reduced the telluric background by 2 orders of magnitude. The samples were measured directly on the endcap of the detectors to maximise the detection efficiency, e.g. 3 % at 1460 keV for K-40, and to obtain around 2000–3000 counts with 2–3 days measurements for this peak. The HPGe detectors had 60 % relative efficiency, and their resolutions were around 0.6 keV, 1.2 keV and 1.8 keV respectively at 46.5 keV, 662 keV and 1460 keV, the characteristic energies of ^{210}Pb , ^{137}Cs and ^{40}K . The energy, resolution and detection efficiency were calibrated with the measurements of radioactive standard sources made of water equivalent epoxy resin containing ^{51}Cr , ^{57}Co , ^{60}Co , ^{85}Sr , ^{88}Y , ^{109}Cd , ^{113}Sn , ^{137}Cs , ^{139}Ce , ^{210}Pb and ^{241}Am to cover the energy range from 22 keV to 1836 keV. No self-attenuation correction of the detection efficiency was needed for ^{40}K due to its high energy, but the detection efficiency must be corrected for the true coincidence summing effects for the calibration measurement. The correction factors calculated with the Gespecor V5 (Sima et al., 2001) software for this counting geometry/detector configuration were 18 % for the 1332 keV peak of ^{60}Co and 25 % for the 1836 keV peak of ^{88}Y , in the same energy range as ^{40}K . The measurement spectra were analyzed by the Genie2000 V3.4 (Mirion) software and provided results with limits of detection for ^{40}K from 4 to 14 Bq/kg dry weight, far lower than the measured activities from 140 to 720 Bq/kg d.w. The expanded total uncertainties around 8–9 % ($k = 2$) were calculated following the ISO/IEC Guide 98-3 (2008) combining the uncertainties on the counting statistics, the detection efficiency, and the sample position. All activity concentration were expressed in Bq/kg_{dry}, noted Bq/kg in this paper.

2.5. Sediment grain size distribution

The grain size distribution was analyzed by laser diffraction

(MASTERSIZER hydro2000G, laser wavelength) on the samples, previously homogenized, moistened if needed, resuspended in water and ultrasonically processed for 1 min. The grain size is calculated from the pattern of the scattered light produced by a dispersed system of particles when the laser beam passes through it. The relationship between particle size and distribution pattern of light is provided by two approximation modes: the Fraunhofer diffraction theory or the Mie scattering theory. Grain size was measured on the GRADISTAT v8.0 such as D10 and D90 (Blott and Pye, 2001); D10, D50 and D90 (μm) represents the maximum grain size of respectively 10 %, 50 % and 90 % of the particle volume, respectively.

3. Results and discussion

3.1. Mineral fertilizer uses in France over the last decades

In France, the use of fertilizers began in the late 1800s, when the development of agriculture became essential in Europe, following the Franco-German War of 1870–1871. Fertilizers were initially imported from abroad then from 1920, potash was produced in Alsace (MDPA, 2018). The consumption of potassic fertilizers increased especially after the Second World War, during the “thirty glorious years”. The country was marked by scientific and technical progress in agriculture and saw the development of extension organizations, advertising and services intended for farmers extolling the merits of chemical fertilizers. One of the leaders of this movement was the Société Commerciale des Potasses d’Alsace (Alsace Potasse Commercial Company, owned by the French State). At this time, fertilizer producers came together to create the National Federation of the Fertilizer Industry and agronomic stations and research centers were created in France to develop and optimize the use of chemical fertilizers (Boulain, 1995). Modern agriculture modifies the theoretical foundations of fertilization. The notions of pH, mineralogy or pedology become elementary characteristics for characterizing soils and allowed to adjust the use of fertilizers. The rapid increase in consumption of potash fertilizers continued until the 1990s. Indeed, from 1990, potash consumption decreases very quickly, in 15 years, deliveries go from almost 2000 kt/yr to around 500 kt/yr (Fig. 2).

This downward trend in the use of chemical fertilizers stems in part from awareness of the ecological consequences of using these fertilizers in excessive quantities in agriculture. This notion is particularly marked by the European agreements which have conditioned agricultural production since the 1970s by considering the quality of drinking water (EEC, 1975, 1980, 1991). In addition, the increase in the price of fertilizers has also contributed to reducing purchases and therefore the use of these fertilizers by farmers (Jouany et al., 1996).

3.2. ^{40}K in cultivated and non-cultivated soils in France over the last forty years (1981–2022)

The ^{40}K activity concentrations datasets from non-cultivated soils ($n = 786$) and cultivated ones ($n = 1228$) collected on the French territories over the 1981–2022 period were extracted from data sets acquired in the scheme of monitoring programs conducted by IRSN. Cultivated soils analyzed included vegetable garden soil, orchard soil, vine soil and outdoor cultivation soil fields while non cultivated soils originate from wasteland soil, marsh soil, pasture or meadow soil, salt meadow soil, coppice soil, bog soil, soil of green space and forest floor. Those did not differ significantly over years and all of them were sampled from the surface to 20 cm depth and were distributed among the French metropolitan territory. Soil samples were compiled whatever their grain size and their organic matter contents, so the data sets explored, statistical analyses performed, and trajectories highlighted integrate the potential effect of these parameters on potassium contents.

At the scale of the French metropolitan territory, ^{40}K activity concentration in cultivated soils displayed significant enriched levels referring to the non-cultivated ones with values ranging over a huge

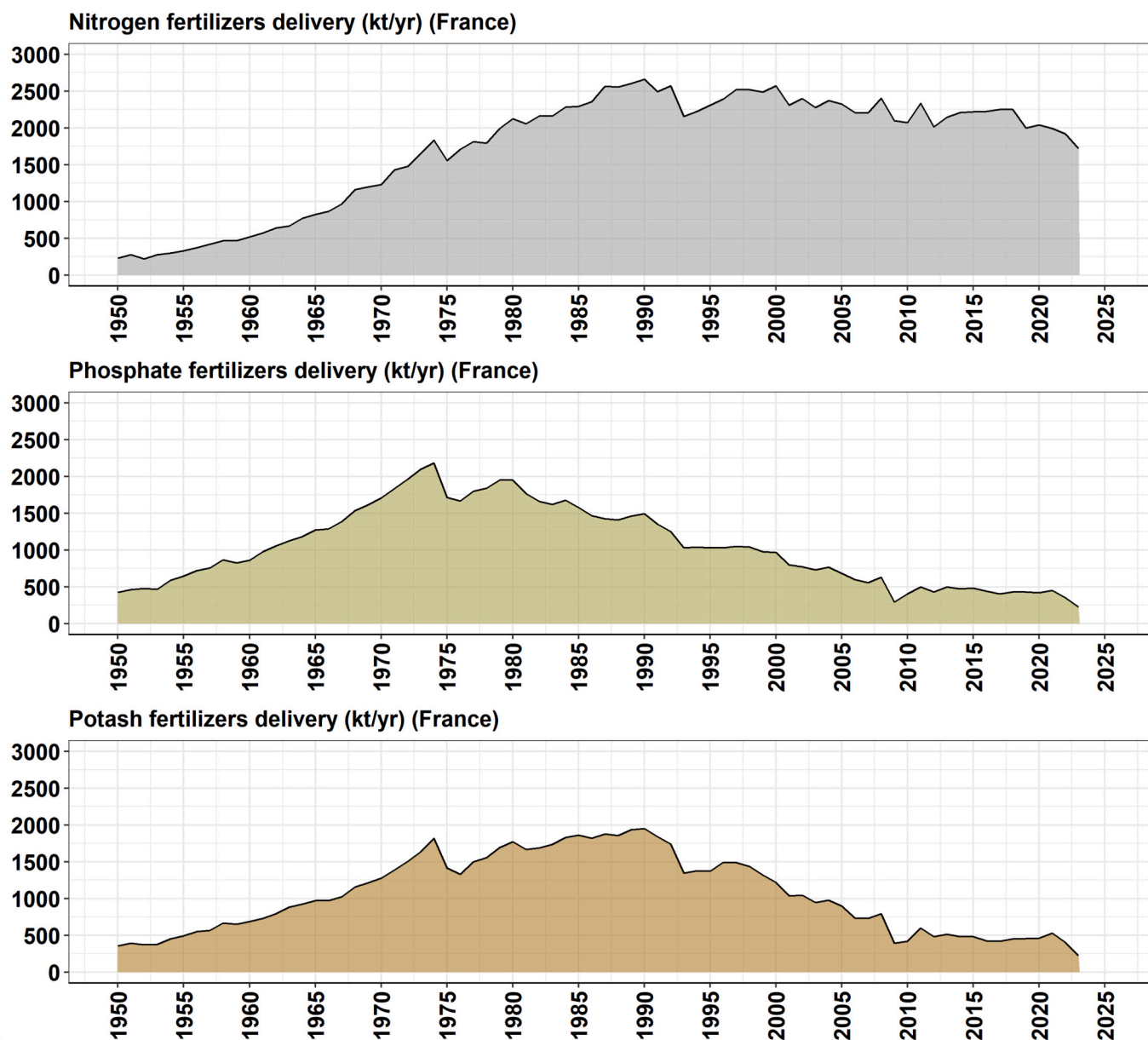


Fig. 2. Annual Nitrogen, phosphate and potash fertilizers delivery (in kilotons per year) in France from 1910 to 2023 (from UNIFA (2022, 2024) and INSEE (1989, 1953–2004)).

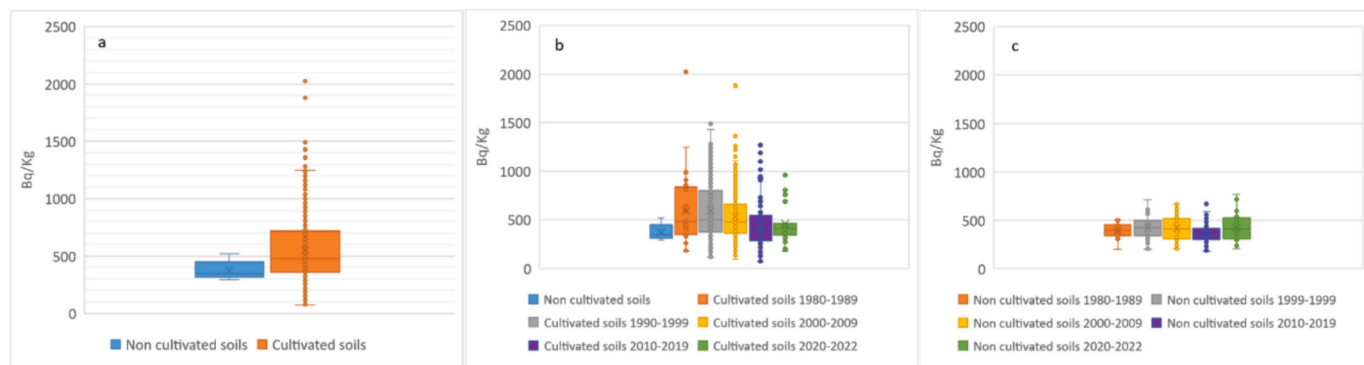


Fig. 3. Statistical reports of ^{40}K activity concentration (Bq/kg) in cultivated ($n = 1228$) and non-cultivated soils ($n = 786$) over the whole period 1981–2022, a, over the various decades (1980s ($n = 39$), 1990s ($n = 554$), 2000s ($n = 513$), 2010s ($n = 95$) and the most recent years (2020–2022, $n = 27$) for cultivated soils, b, and over the various decades (1980s ($n = 21$), 1990s ($n = 53$), 2000s ($n = 85$), 2010s ($n = 62$) and the most recent years (2020–2022, $n = 13$) for non-cultivated soils, c.

range from 77 to 2026 Bq/kg (mean 552 Bq/kg) and from 314 to 520 Bq/kg (mean 375 Bq/kg), respectively (Fig. 3, a). These ranges of value cannot be directly compared to the world average value of activity concentration for ⁴⁰K in soil (140–850 Bq/kg, mean value 370 Bq/kg, UNSCEAR (2000)) because in this latter case both categories of soil, virgin and fertilized, was mixed to estimate the world average range and the period covered by the dataset used was not reported. Among the period covered by the dataset explored in our study, the 1980s revealed the highest ⁴⁰K activity concentrations in cultivated soils (185 to 2026 Bq/kg, mean 590 Bq/kg). This period was followed by a significant and progressive decrease of ⁴⁰K contents until the most recent years (2020–2022) with values reaching those currently registered for non-cultivated soils (Fig. 3, b). This decreasing trend over time was not observed in the case of non-cultivated soils (Fig. 3, c). These results clearly underline the imprint of fertilizer uses over time on cultivated soils at the scale of the whole French metropolitan territory.

3.3. ⁴⁰K temporal trajectories in riverine sediments over the last hundred years (1920–2022)

⁴⁰K activity concentrations in riverine sediments were reconstructed from sediment cores collected at the downstream sections of the Loire, Moselle, Rhine, Rhone, Meuse and Seine rivers (Fig. 4). With an exception for the Seine River collected in a continuously submerged secondary channel, all the cores were collected at the downstream part of the rivers onto alluvial margin displaying close hydrodynamic and depositional conditions, where sediment deposition was as continuous as possible over the last decades, and where deposits were mostly composed of fine grain sediments, as previously described in Eyrolle et al. (2024). This approach was used to restrain biases on element distributions over time and space due to hydrodynamic variations and to improve cross-comparison of the samples. Eyrolle et al. (2024) demonstrated that the great majority of sediments was mainly deposited by uniform to graduated suspension (60–70 μm < D99 < 400 μm) whatever the studied site, with some exception for few sandy layers deposited from graduated suspension with rolling to rolling (D99 > 400 μm and D99 > 1100 μm).

Contrarily to the soil datasets covering the last forty years, the periods of time covered by the sedimentary cores embraced a longer period, i.e. at least the seventy last years in the case of the Seine River, to

more than the last hundred years for the Rhine and Moselle rivers. Apart from the Loire and Moselle rivers which displayed relatively high ⁴⁰K contents before the 1960s, almost all the systems revealed a similar general temporal trend. The latter was characterized by ⁴⁰K activity concentrations initially close to those of the referential non-cultivated soils collected in the catchments, for the period before the 1960s, followed by an increase until the middle or end of the 1980s. Then, ⁴⁰K activity concentrations in sediments turned back towards the referential values of non-cultivated soils for all the rivers, except the Loire River which displayed overall constant values until the recent years, lower than those observed in the 1960s but higher than those of referential non cultivated soils. These general trends obviously suffered of a huge variability in ⁴⁰K contents most probably due to the variability of the grain size, origin, and nature of the deposited sediments. The trend was particularly obvious for the Moselle (post 1955) and Rhine rivers, also for the Rhone and Seine rivers although these latter rivers were tarnished by an important variability in ⁴⁰K contents. No significant temporal trend was observed in the case of the Meuse River. Finally, the Loire River showed the highest ⁴⁰K activity concentrations whatever the period (550 ± 48 to 900 ± 72 Bq/kg), significantly above the non-cultivated soils referential values in its catchment (171 ± 15 to 592 ± 42 Bq/kg), with a slight maximum (680 ± 45 Bq/kg) at the end of the 1970s for the period post 1960. Enrichment factors, referring to the mean ⁴⁰K activity concentrations measured in the soils of the various catchments of each studied basin, showed that since the 1960s, the Loire and the Seine riverine sediments were the most enriched ones (EF_{max} = 1.93 in 1979, and EF_{max} = 1.82 in 1992, respectively), followed by the Moselle, Rhine and Rhone systems (EF_{max} = 1.35 in 1986, EF_{max} = 1.30 in 1986, and EF_{max} = 1.39 in 1992, respectively). The Meuse sediments were below 20 % of enrichment whatever the period (Fig. 5). Over the 1980s–1990s, the grain size of deposited sediments within the different archives was rather similar (mean D50 = 16.3, 28.8, 21.8, 35.4, 20.7 and 15.5 μm for the Loire, Seine, Rhone, Moselle, Rhine and Meuse rivers, respectively) and had therefore a negligible role on EF_{max} values. Over the last decade, EF values were close to 1 for all the rivers with an exception for the Loire River which showed a stable EF value higher than 1.5. In this latter case, the relatively high ⁴⁰K activity concentration in the sediments of the Loire River when compared to other rivers, even for the fine particle grain size and the more recent years, would suggest either that ⁴⁰K enriched minerals were also represented in the finest particles or that the Loire River resilience faced to potassic fertilizers uses in its catchment was not yet reached.

Finally, the EF_{max} classification of rivers was compared to the proportion of agricultural areas in their catchments (Fig. 6). Even though the relationship was not significant (R² = 0.57), the results indicate that EF_{max} globally increases when the proportion of agricultural areas in the catchment rises. The Loire and the Seine basins, where the highest EF_{max} were registered, displayed the highest proportion of agricultural soils.

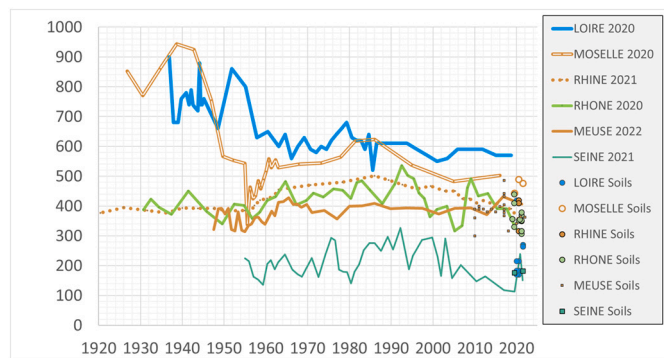


Fig. 4. Temporal trajectories of ⁴⁰K activity concentration in sediments (Bq/kg) of the Loire, Moselle, Rhine, Rhone, Meuse and Seine rivers reconstructed from sediment cores and ⁴⁰K activity concentrations measured in non-cultivated soils of each studied basin distributed among their various catchments; These latter data were used as referential values to calculate ⁴⁰K enrichment factors (EF⁴⁰K) for the various basins and ranged from 171 ± 13 to 593 ± 47 Bq/kg (mean = 352 ± 155 Bq/kg) for the Loire basin; from 443 ± 37 to 489 ± 42 Bq/kg (mean = 463 ± 23 Bq/kg) for the Moselle basin; from 317 ± 26 to 410 ± 33 Bq/kg (mean = 375 ± 53 Bq/kg) for the Rhine basin; from 307 ± 25 to 440 ± 38 Bq/kg (mean = 384 ± 36 Bq/kg) for the Rhone basin; from 300 ± 23 to 486 ± 41 Bq/kg (mean = 384 ± Bq/kg) for the Meuse basin and from 176 ± 13 to 182 ± 15 Bq/kg (mean = 179 ± 8 Bq/kg) for the Seine basin;

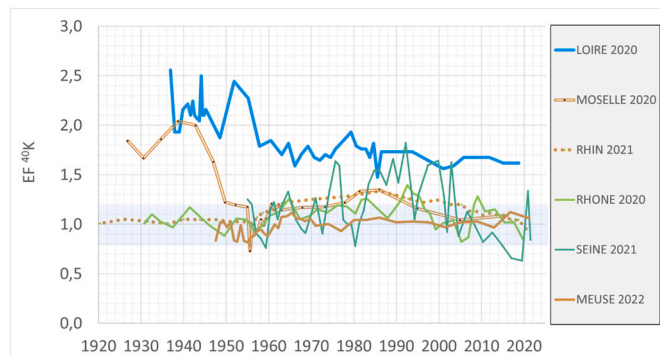


Fig. 5. Temporal trajectories of enrichment factors of ⁴⁰K activity concentration in sediments (EF⁴⁰K) for the Loire, Moselle, Rhine, Rhone, Meuse and Seine rivers; the blue band represents the area among which EF⁴⁰K is below 20 %.

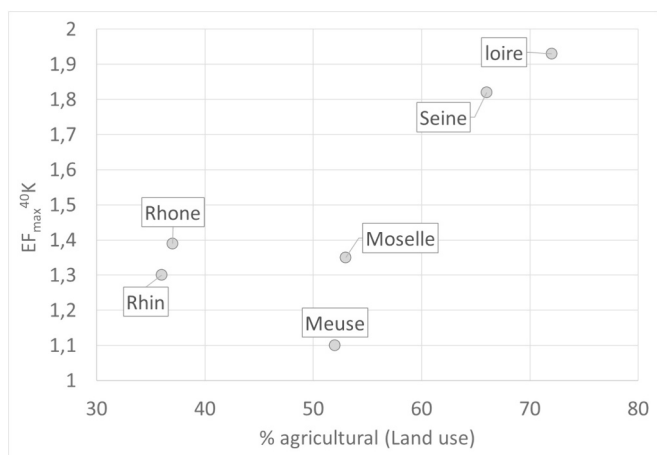


Fig. 6. Maximum enrichment factors of ⁴⁰K activity concentration in sediments (EF_{max}^{40K}) versus the amount of agricultural land use in the recent decade for the Loire, Moselle, Rhine, Rhone, Meuse and Seine rivers.

The correlation between these two parameters would be probably enhanced by considering the agricultural surfaces during the 1980s rather than those compiled over the recent years because of land use change over time. Unfortunately, these data were not available for all the studied rivers.

3.4. ⁴⁰K dependency upon the grain size and nature of sedimentary particles

Most of particle reactive elements exchange with solid surface of naturally occurring solid particles. Some of them are also directly constitutive of the solid particle themselves. This is the case for ⁴⁰K which is either adsorbed onto sedimentary particles through solid/solution exchanges with the surrounding waters or inherited from soil erosion particles and included in the crystal lattice of detrital particles. The distribution coefficient between the solid and dissolved phases (KD) was estimated to $11,000 \pm 2000$ L/kg_{dry} in the case of the Rhone River (Eyrolle et al., 2020) and to range from 566 to 69,500 L/kg_{dry} at the world scale (geometric mean = 19,300 L/kg_{dry}, Boyer et al., 2018). This coefficient value is of the same order of magnitude as those reported for trace element isotopes such as ⁵⁴Mn, ⁶⁰Co and ¹³⁷Cs (Eyrolle et al., 2020) underlying that ⁴⁰K significantly adsorbs onto sedimentary particles. In soils, exchangeable potassium accounts for 1–2 % of total potassium and is electrostatically bound on the surfaces of clay minerals and humic substances from which it can be released quickly into the soil solution (Bijay-Singh and Sapkota, 2023). Potassium, as a bioelement, is constitutive of living and detrital organisms and in this way organic matter may contain varying amount of potassium depending on its nature, i.e. fresh or detrital as an example (Andrews et al., 2021). Detrital compounds are most generally depleted in soluble elements. Unamended soils and more especially riverine sediments are mainly composed of detrital organic matter and only few amounts of potassium can be driven by organic compounds themselves in such natural environmental components. In such systems, organic matter is also known to compete with numerous elements, including potassium, regarding the available exchangeable surface sites developed by the mineral particles and, most generally, organic matter content increase with the decreasing size of particles (e.g. Bergamaschi et al., 1997; Marengo et al., 2006). The sediments strata investigated in this work contain <8 % of total organic carbon with a mean content of 2.5 % (SD = 1.4 %, n = 252) and the particle size range over a rather straight range (Eyrolle et al., 2024), so the organic matter content was not considered here to significantly alter the temporal trajectories observed.

Apart from surface sorbed ⁴⁰K, several naturally occurring minerals

such as alkaline feldspars (orthoclase, microcline), muscovite and biotite or illite minerals contains significant amounts of potassium in their lattice, including ⁴⁰K, because of their telluric origins. Non-exchangeable and structural potassium, i.e. strongly bound to the minerals through electrostatic forces as in the case of illite or muscovite, or incorporated in the crystal lattice structure of minerals as K-feldspars, account for 96–99 % of total soil potassium, and are considered to be slowly- and potentially-available potassium sources for plants, respectively. Most generally, mass concentration due to loosen adsorption onto the surface of solid particles decreases with the rising grain size while the grain size effect is negligible for particle constitutive elements. In our study, no significant trend with the grain size was observed for the Meuse, Rhone and Rhine rivers (Fig. 7). In contrast, in the case of the Seine River, ⁴⁰K activity concentration in sediments showed a general trend to decrease when the particle size increased underlining that ⁴⁰K was mainly sorbed onto particles. Finally, for the Loire and Moselle rivers, ⁴⁰K activity concentration displayed an opposite tendency with the sediment grain size most probably due to the presence of naturally occurring ⁴⁰K enriched sandy minerals such as K-feldspars which were clearly identified in the sandy strata of the archives.

Sandy sedimentary strata were observed at the depth of the Loire and Moselle sedimentary archives, i.e. below 130 cm (1957) and 122 cm (1950), respectively (Eyrolle et al., 2024). This would explain the relatively high ⁴⁰K contents observed before 1957 and 1950 respectively in the Loire and Moselle rivers. In the case of the Loire River, Copard et al. (2022) underlined a drastic change in the content of petrogenic organic carbon (POCp) in the sediments of the river from the 1960's. The authors reported that while the period from 1923 to 1959 indicated very low POCp content (0.01 wt%), in contrast, the period from 1961 to 2016, revealed a POCp amount of 0.59 wt%. This difference in POCp content over these two periods of time was interpreted as a major change in sediment sources due to land use management and the conversion of grassland into agricultural area. In the case of the Moselle River, Eyrolle et al. (2024) reported disrupted profiles of both ¹³⁷Cs, ²⁴¹Am and ²¹⁰Pb_{xs} up to 112.5 cm depth (after 1955) most probably due to a discontinued sedimentation explained either by a partial remobilization of previously deposited sediments before bank stabilization or by sediment inputs from varying origins. Indeed, the emergence of the “Bird’s Island”, in front of the coring site, in the late 1950s, due to the Moselle channelization to protect from erosion the Saint Michel church overhanging the steep valley side at Berg-sur-Moselle, could explain this disruption. Finally, the reconstruction of floods for the Moselle River performed by Delus et al. (2023) indicated the occurrence of an extreme flood in 1947 which would explain the thick ⁴⁰K-enriched sandy layer below 127 cm (before 1950).

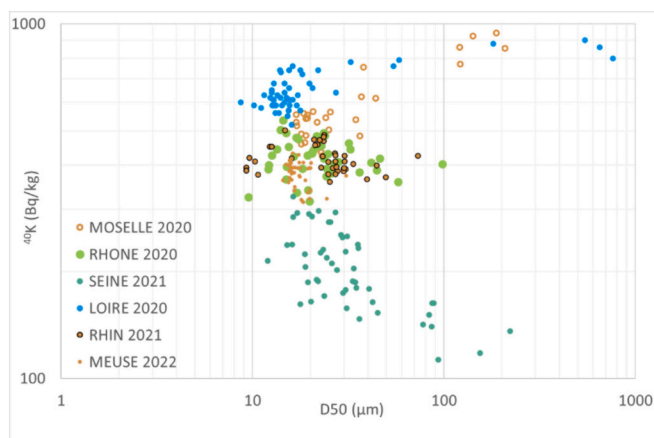


Fig. 7. ⁴⁰K activity concentration in sediments of the Loire, Moselle, Rhine, Rhone, Meuse and Seine rivers with the mean grain size (D50).

3.5. Anthropogenic legacy from potassic fertilizers

The temporal trajectories of ^{40}K activity concentration were finally directly compared to the chronicles of potassic fertilizer delivery in France (Fig. 8). All the data (A) were normalized (A_{norm}) with extreme values (minimum value, $\min(A)$ and maximum value, $\max(A)$, eq.1) to improve their comparison.

$$A_{\text{norm}} = (A - \min(A)) / (\max(A) - \min(A)) \quad (1)$$

In the case of the Loire and Moselle rivers the data associated to the period before 1957 and before 1950, respectively, were discarded

because of their high content in sandy particles naturally enriched in ^{40}K . The comparison of the normalized data sets showed very similar trajectories between the pressures, i.e. potassic fertilizer delivery, and the environmental response, i.e. ^{40}K activity concentration in sediments, clearly highlighting that the uses of potassic fertilizers on the catchments directly imprint the riverine sediments of most French rivers. Our results also highlighted that the environmental resilience face to this contamination type is rather fast in rivers as ^{40}K levels decreased immediately after the decreases of the deliveries. This is most probably due either a rapid consumption of potassium by crops into agricultural surfaces, vertical migration of soluble potassium in soils and/or dilution

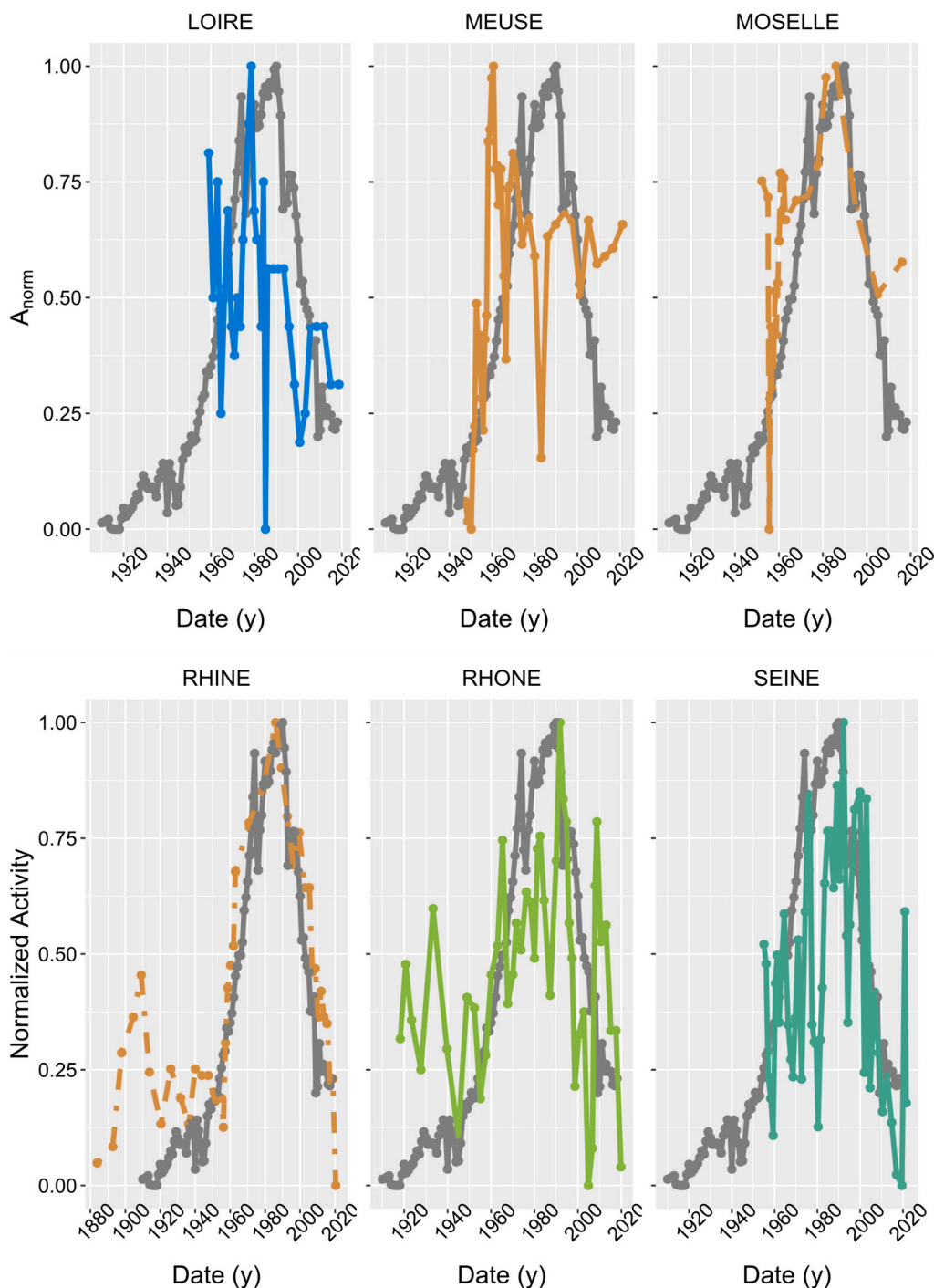


Fig. 8. Temporal chronicles of ^{40}K concentration activity in sediments of the of the Loire, Moselle, Rhine, Rhone, Meuse and Seine rivers and Potassic fertilizer delivery (in grey) normalized to extreme values.

in freshwaters after solid/solution exchanges. Finally, the results suggest that excess ^{40}K delivered by anthropic activities on the catchment can be neglectable when compared to ^{40}K activity concentrations displayed by some naturally occurring minerals.

4. Conclusions

Inorganic fertilizers were widely used around the world to counter-part potassium depleted agricultural soils. In Europe, Potassic fertilizers delivery significantly increased during the 1950s until the end of the 1980's when they culminated before they drastically and continuously decreased during the following decades. In France, cultivated soils contained 50 % more ^{40}K than non-cultivated soils during the peaking potassic fertilizer delivery in the 1980s, on average, with maximum excess reaching 600 %. Temporal trajectories of ^{40}K contents in riverine sediments of large French rivers reconstructed from sediment cores highlighted that fertilizer uses imprinted river systems. Maximum enrichment factor, ranging from 30 to 90 % in the 1980s, were registered in fine-grained sediments at the downstream sections of the Rhine = Moselle < Rhone < Seine < Loire rivers. These would be related to the percentage of agricultural surfaces in the catchment. Additionally, excess ^{40}K contents in soils and river systems originating from inorganic fertilizer uses onto agricultural surfaces rapidly declined when fertilizer deliveries were reduced underlying no long-term persistence and a rapid resiliency of soils and riverine sediments face to ^{40}K fertilizer derived inputs.

CRedit authorship contribution statement

Frédérique Eyrolle: Writing – review & editing, Writing – original draft, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Amandine Morereau:** Writing – original draft, Investigation, Formal analysis. **Mathilde Zebracki:** Writing – review & editing, Validation, Investigation. **Valérie Nicoulaud Gouin:** Writing – review & editing, Writing – original draft, Software, Methodology. **Hugo Lepage:** Writing – review & editing, Writing – original draft, Software, Methodology. **Anne de Vismes:** Writing – original draft, Methodology. **Anne Meyer:** Writing – original draft, Methodology. **Emmanuelle Montarges-Pelletier:** Writing – review & editing, Validation, Formal analysis. **François Chabaux:** Writing – review & editing, Validation, Resources, Methodology. **Alexandra Coynel:** Methodology. **Maxime Debret:** Methodology. **Franck Giner:** Methodology. **Cécile Grosbois:** Writing – review & editing, Supervision. **Rodolfo Gurriaran:** Resources. **David Mourier:** Methodology. **Laurence Lestel:** Validation.

Declaration of competing interest

The authors declare that there are no relevant financial or non-financial competing interests to report.

Data availability

Data will be made available on request.

Acknowledgements

The authors are grateful to the ANR TRAJECTOIRE project (ANR-19-CE3-0009, 2020–2025) and IRSN for financial support.

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