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Amélie Humbrecht, Anaëlle Simonneau, Thomas Thiebault, Gauthier Bernier-Turpin, Claude Le Milbeau, et al.. Effect of sediment composition and accumulation on pharmaceutical product spatial distributions at the suburban pond scale (Beulie pond, SNO Observil, France). *Applied Geochemistry*, 2025, 190, pp.106487. <10.1016/j.apgeochem.2025.106487>. <insu-05155910>

HAL Id: insu-05155910

<https://insu.hal.science/insu-05155910v1>

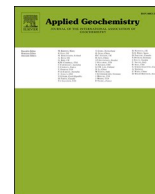
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Effect of sediment composition and accumulation on pharmaceutical product spatial distributions at the suburban pond scale (Beulie pond, SNO Observil, France)

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ARTICLE INFO

Editorial handling by: Elisa Sacchi

Keywords:

Pond sediment
Organic matter
Kaolinite
Pharmaceutical products
Spatial distribution

ABSTRACT

Pharmaceutical products (PPs) are found in several compartments of the environment, and are mostly emitted by wastewater treatment plants effluents. Their occurrence in the particulate phase, in opposition with the dissolved one, also promotes their occurrence in retention areas, where particles transported by streams settle. The study focuses on understanding how different constituents of pond sediment are distributed within a suburban pond, revealing patterns or hotspots of PPs accumulation. Results confirmed the heterogeneous spatial distributions of the granulometric fractions, total organic carbon, quantitative palynofacies, crystalline phase distributions and PPs contents. The delta preferentially concentrates total organic carbon (14.5 ± 2.2 %), and particularly terrigenous organic matter and neutral PPs, while the main decantation area accumulates mostly fine particles (58.2 ± 7.7 %), kaolinite, algal organic matter and cationic PPs. The potential role played by OM and kaolinite in PPs adsorption is supported by their respective spatial trends at the pond scale. Further attention should be paid to surface sediments components and PPs sensitivity to seasonal variations, especially in terms of flow, pH and oxygenation of the water-column. This spatial approach allowed to identify preferential accumulation and concentration areas within the pond, where the following extensive characterization of interface sediments highlighted the factor likely to influence PPs trapping within the pond.

1. Introduction

Over the last decades, the fate of contaminants of emerging concerns in the environment has become one of the most important scientific issues in terms of environmental and human health safety (Gerbersdorf et al., 2015; Duarte et al., 2022; Aftab et al., 2023). Indeed, their continuous production and therefore emission, even at low concentrations, is likely to damage the quality of ecosystems (Halling-Sørensen et al., 1998; Nannou et al., 2020) due to the persistence of some of those substances (Hernando et al., 2006). Organic contaminants, typically

pharmaceutical products (PPs), can be found in different compartments of the environment, such as in agricultural soils (Monteiro and Boxall, 2009), river bed-load sediments (Romanić et al., 2023; Castaño-Ortiz et al., 2024), and suspended particulate matters (SPM, Lahti and Oikari, 2011; da Silva et al., 2011; Aminot et al., 2015), regardless of the scale of the watershed (from a few to thousands of km²). Besides, small watersheds are considered particularly vulnerable (Boulard et al., 2020) because of their reactivity to flash flood events (Wang et al., 2019). In suburban, or urban, environments, waste water treatment plant effluents are integrated into the natural watershed functioning. They

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<https://doi.org/10.1016/j.apgeochem.2025.106487>

Received 3 March 2025; Received in revised form 6 June 2025; Accepted 28 June 2025

Available online 3 July 2025

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represent one of the most important sources of anthropogenic contaminants (Jacob et al., 2020; Ledieu et al., 2021; Thiebault et al., 2021).

The behavior of contaminants emitted within watersheds can lead to different fate scenarios and the number of organic molecules detected in the environment is constantly increasing. Non-persistent contaminants are often subjected to early degradation, while pseudo-persistent contaminants can be transported far from their sources depending of their partition coefficients (Turner and Millward, 2002), either because of their resistance to degradation or their sorption properties to SPM considered as main pollutant by the Water Framework Directive, 2000 (DCE, 2000). The Stockholm Convention (Mbengue, 2001) listed "Persistent Organic Pollutants" (POPs) that shall be surveyed. Recently, Jones (2021) also pointed the necessity to consider other "POPs", such as PPs, which can lead to damaging consequences for hydrosystems because of their continuous emission in the environment (Halling-Sørensen et al., 1998). PPs are known to be mainly hydrophilic, explaining why most studies have focused on the aqueous phase (Bound and Voulvoulis, 2006; Wilkinson et al., 2022). However, the particulate matter transported at the catchment scale (i.e. SPM), can act as a carrier phase for contaminants via sorption reactions (Al-Khazrajy and Boxall, 2016), including for hydrophilic substances such as PPs.

SPM are particles whose sizes range between 0.45 μm and 1800 μm ; transported in the water-column; mixed of small aggregates including organic matter (OM), and are therefore good candidates for carrying contaminants. Some of them reach the outlet, but others can also accumulate within water retention areas. The latter therefore represent a rupture in stream connectivity, promoting the decantation of particles, depending on their granulometry, mineralogy and interaction with organic matter. As a consequence, an increasing number of studies are looking for PPs contents in sediments (Aminot et al., 2015; Fairbairn et al., 2015; Cantwell et al., 2018), especially for their temporal distribution in sedimentary archives collected in natural or artificial basins (Thiebault et al., 2017, 2021). The spatial distribution of contaminants in retention areas is usually vertically conducted, with the sampling of sediment cores, also named archives, in order to provide a temporal reconstitution in one area at the retention area scale. High spatial resolution samplings are only performed in a few studies (Lara-Martín et al., 2015; Cantwell et al., 2018). This can lead to a "dilution" of potential hotspots of contaminants in those archives. Furthermore, sediment composition, including its granulometry, geochemistry, and mineralogical properties, can also be spatially heterogeneous at retention area scale. As these sediment components are potential carriers of contaminants, it is necessary to compare their spatial distributions with those of contaminants, in order to understand how both can be linked.

In this context, the present study attempts to understand the spatial distribution of PPs contents at a retention area scale, which is located in the center of a suburban watershed. The purpose of the present study is particularly to discuss the representativeness of water-sediment samples in terms of contaminant contents in water bodies. The objectives are (i) to chemically and physically characterize the particulate phase at the pond scale, (ii) to measure and draw maps of the bulk matrix components, as well as contaminants distribution, and (iii) decipher the factors controlling contaminant heterogeneous distribution at pond scale. This work therefore used a step-by-step approach. First, a high spatial resolution sampling of surface sediments at the pond scale was performed over 5 years. This was followed by a characterization of surface sediments components. This allowed the identification of hotspots of both surface sediments reactive matrices and PPs and gave new insights about the origin of sediment matrices and PPs spatial distribution at the pond scale.

2. Materials and methods

2.1. Site description and sampling strategy

2.1.1. Study area

The Beulie pond represents a surface area of about 4000 m^2 . The catchment area drained by the pond covers a surface area of 6.3 km^2 and is located in the northeast part of Orleans (France). It is characterized by an upstream/downstream anthropogenic gradient, along which soil occupation evolves from forest to urban areas, industry, and apple orchards. Its tributary, the Egoutier stream, is fed from rainwater and also two waste-water treatment plant effluents coming from the central army pharmacy and a psychiatric hospital (Fig. 1). Previous studies conducted within the same catchment (Ledieu et al., 2020, 2021) quantified Atenolol (ATE), Tramadol (TRA), Metoprolol (MTP), Carbamazepine (CBZ), Oxazepam (OXA), Diazepam (DIA) and Paracetamol (PAR) in aqueous and particulate phases and notably in surface sediments collected within the Beulie pond.

2.1.2. Sampling strategy

Between September 2018 and September 2023, 43 surface sediments were collected within the Beulie pond using an Ekman grab. The thickness of the sampled sediment layer represented between 5 and 10 cm.

Sampling campaigns between September 2018 and September 2022 were dedicated to a characterization of surface sediment component spatial distributions at the pond scale. TOC spatial distribution was particularly investigated. For samples collected in 2021, PPs quantification and laser granulometry were also performed, in order to determine the spatial distributions of PPs, and of surface sediment granulometric fractions, especially the fine one (<63 μm).

The results obtained for the 40 surface sediments collected between 2018 and 2022 illustrated a spatial heterogeneity of TOC, PPs and granulometric fraction contents at the pond scale. In the light of this observation, a new sampling was performed in September 2023, in 3 areas of the pond being representative of this spatial heterogeneity: the delta (45-BE23-BE1 #0), the upstream area of the pond (45-BE23-BE2 #1) and the main decantation basin of the pond (45-BE23-BE3 #2). These samples were subjected to an extensive characterization, including TOC and PPs quantification, and additionally X-ray powder diffraction (XRD) and quantitative organic petrography (QOP), in order to better characterize the mineralogy and the organic matter of the bulk matrix. The physical-chemical properties of the water-column were also investigated. The sampling of 2023 aim was to determine the origins and the parameters driving the spatial heterogeneity of the bulk matrix component and PPs contents at the pond scale.

2.2. Water-column characterization

The physical-chemical properties of the water-column were investigated in the 3 areas chosen for the sampling of September 2023, in order to compare the physical-chemical conditions at the water-sediment interface with corresponding sediment sample characteristics. The pH, the electrical conductivity, the dissolved O_2 concentration and the temperature were measured each 5 cm from the water-surface to the water-sediment interface. The probes were provided by WTW. The pH probe was calibrated for 3 points with standard calibration solutions (4.0, 7.0, 10.01). The electrical conductivity probe was calibrated with a KCl solution at 1413 $\mu\text{S}/\text{cm}$.

2.3. Characterization of OM, granulometric distribution and crystalline phases in surface sediments

2.3.1. Organic matter characterization

Bulk geochemical study of the organic matter was obtained by Rock-Eval pyrolysis to characterize the organic content of natural samples by

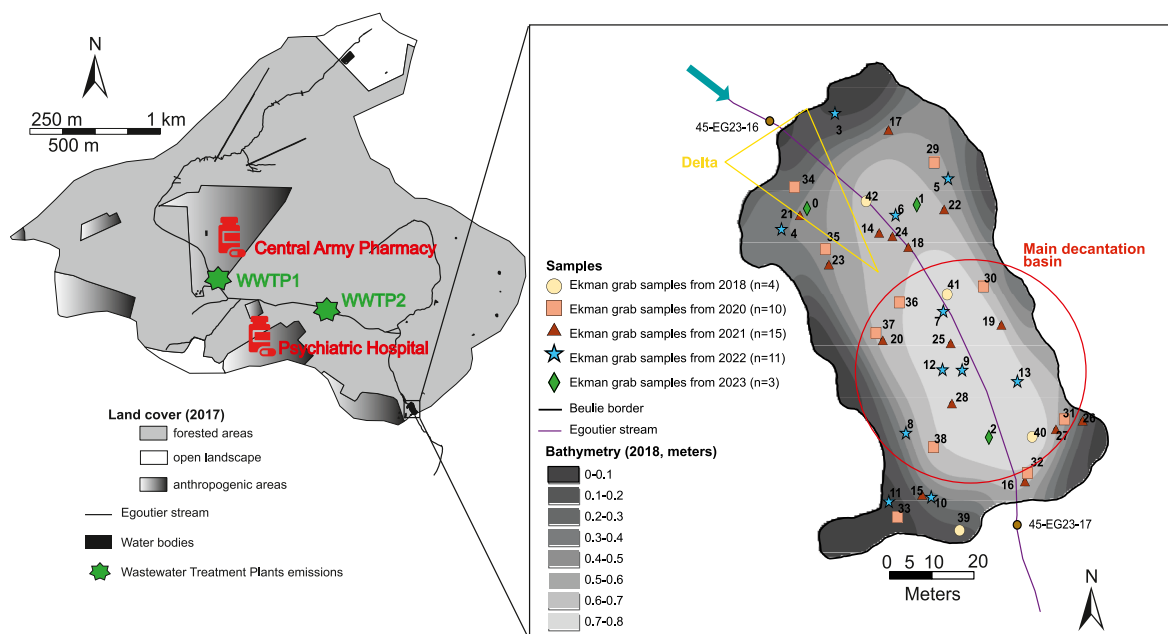


Fig. 1. Map representing the Beulie pond catchment area with information about soil occupation collected from Corine Land Cover data from 2017. The Egoutier stream is represented by the black continuous line. The two wastewater treatment plants connected to 1- the central army pharmacy and 2- a psychiatric hospital are represented as green stars. A zoom is made on the Beulie pond. The bathymetric map is represented. 43 Ekman grab samples, collected between September 2018 and September 2023 are represented on the map. Sample names on the map are represented by a number (0–42) for purposes of simplification.

thermal cracking and to quantify the amount of hydrocarbons that escape from the studied sample. Analyses were performed using Rock-Eval 6 Turbo (Vinci Technologies). The TOC (%) and the Hydrogen Index ($HI = (S2 \cdot 100) / TOC$) expressed in $mgHC \cdot g^{-1} \cdot TOC$, with S2 corresponding to the peak obtained for pyrolysis products from cracking OM, Behar et al., 2001) are the two main parameters frequently used to characterize soil organic matter (Disnar et al., 2003; Sebag et al., 2006) or to identify the OM origin in lacustrine environments (Talbot and Livingstone, 1989; Ariztegui et al., 2001; Simonneau et al., 2014). The TOC represents the amount of organic carbon in samples and the HI corresponds to the chemical quality of the organic compounds. Its decrease highlights the oxidation of the matter in the sediment or a contribution of terrestrial material (Ramanampisoa and Disnar, 1994).

QOP was performed on the 2023 sample set. QOP consists of the optical identification and quantification of the organic constituents present in a constant volume of sediment (1 cm^3) or in 1 g of soil, after elimination of carbonate and silicate phases by hydrochloric and hydrofluoric attacks (Graz et al., 2010). Components are characterized by their optical properties (color and reflectance), their forms (amorphous or figurative) and their origins (algal, phytoclastic or fossil).

2.3.2. Granulometric distribution

The granulometric distribution is represented here by clay ($< 2 \mu\text{m}$), fine silt ($2\text{--}20 \mu\text{m}$), coarse silt ($20\text{--}63 \mu\text{m}$), fine sand ($63\text{--}250 \mu\text{m}$) and coarse sand ($250\text{--}1800 \mu\text{m}$) contents, according to the Udden-Wentworth scale, calculated for 2021 sample set. The granulometric distribution was determined using laser diffraction particle size analyzer (Beckman Coulter, LS 13 320 XR). The fine particles fraction (FP, i.e. particle size $\leq 63 \mu\text{m}$), was particularly investigated in this study to track the silty to clay fraction. The samples were dried at 45°C , then crushed in an agate mortar. A few milligrams of samples were left on a cell filled with demineralized water. Potential aggregates were removed with ultrasonication. A laser ray is emitted and its reflection depends on particles size, which finally allows to get the particle size as a function of the volume occupied in the cell.

2.3.3. X-ray diffraction analysis

Crystalline phases identification and quantification, along with the determination of amorphous phase content, were performed using XRD. All measurements were conducted using X'Pert PRO diffractometer (Malvern PANalytical, Netherland) operating in parafocussing Bragg-Brentano geometry. The diffractometer was equipped with iron-filtered $\text{Co K}\alpha$ radiation source and fast X'Celerator detector. First, to identify and quantify crystalline phases, bulk powder samples were homogenized in an agate mortar. Then, approximately 100 mg was equally spread on a zero-background Si slide and gently pressed to ensure proper positioning in the sample holder for XRD analysis. Next, the amorphous phase content was determined using the internal standard method (Madsen et al., 2011) by adding 10 mg of well-crystallized ZnO powder to 90 mg of the sample, followed by mixture homogenization for 10 min in an agate mortar and spread on a sample holder as mentioned before. Finally, to identify phases associated with organic matter, samples were reanalyzed after OM removal. Sediment samples OM was digested using 6 % hydrogen peroxide. Samples were then rinsed with ultrapure water then centrifuged, overnight dried at 45°C , and finally crushed in an agate mortar to obtain a homogeneous powder.

XRD patterns from all analyzed samples were acquired in 2θ range from 5 to 105° . The data were processed using HighScore Plus software in conjunction with the PDF-5+ and ICSD databases. The calculation of amorphous content and quantitative phase analysis was performed using the Rietveld refinement (Rietveld, 1969).

2.4. Quantitative analysis of pharmaceutical products

PPs were quantified using Liquid-Chromatography coupled with a Mass Spectrometer. Sediment samples were prepared and analyzed following the method described by Le Gaudu et al. (2022). Seven PPs were quantified in this study: 3 cationics: TRA, ATE and MTP; and 4 neutrals: PAR, CBZ, DIA and OXA. Their characteristics at the pH range of the Beulie pond water-sediment interface (between 7.0 and 7.7 in September 2023) are given in Table 1. $1.0 \pm 0.1 \text{ g}$ of sample was spiked with isotopically labeled internal standards, and 50 ng of each were added (LGC Standards), mixed with 1 g of EDTA and then extracted with

Table 1

PPs dissociation constants (pKa), dominant forms at pH between 7 and 8 and octanol-water partition coefficient ($\log K_{ow}$).

	pKa	Principal charge state at Beulie pond pH	Persistence in the aquatic environment	$\log K_{ow}$
Atenolol	9.6 ^a	Cationic	Moderate ^h	0.16 ^f
Tramadol	9.4 ^b	Cationic	Moderate ⁱ	3.01 ^f
Metoprolol	9.7 ^c	Cationic	Moderate ^j	1.79 ^g
Carbamazepine	2.3 ^d	Neutral	High ^h	2.45 ^f
Oxazepam	10.6 ^e	Neutral	High ^k	3.34 ^f
Diazepam	2.9 ^f	Neutral	Moderate ^k	2.70 ^f
Paracetamol	9.5 ^e	Neutral	Low ⁱ	0.46 ^f

^a Amirdehi et al. (2017).

^b Cisneros-Covarrubias et al. (2022).

^c Li et al. (2019).

^d Correia-Sá et al. (2021).

^e www.drugbank.ca; Knox et al. (2024).

^f Thiebault et al. (2021).

^g Thiebault et al. (2017).

^h Bendz et al. (2005).

ⁱ Lam et al. (2004).

^j Zhang et al. (2020).

^k Löffler et al. (2005).

MeOH using pressurized liquid extraction (ASE 350, Thermo). The residue was recovered with ultra-pure water, and following solid-phase extraction was performed using Chromabond-HLB columns (6 mL × 150 mg × 30 µm, Macherey-Nagel). PP were eluted using 2x5mL of MeOH, and then dried under nitrogen flow, and filtered at 0.22 µm (Nylon filter, VWR). MeOH was used again to recover extracts, before their injection in 1200 SL HPLC system (Agilent). An electrospray source (ESI) was used under positive mode.

3. Results

3.1. Characterization of surface sediment matrices

3.1.1. Organic matter characteristics

Whatever the water-sediment interface sample, the S2 peak measured with Rock-Eval pyrolysis fluctuated between 44.4 and 89.0 mgC/g of dried sediment. These results suggest that the OM accumulated into the Beulie pond is quite homogenous, made of mixed origin (Simonneau et al., 2013), composed of more or less oxidized terrestrial and algal OM (Fig. 2A). The mean TOC content at the pond scale is equal to 12.7 ± 2.0 % (Table S1). Sediments samples at the pond scale can be considered as being rich in organic carbon (Ittekkot, 1988), however, TOC distribution within the Beulie pond is characterized with a gradient, decreasing from the delta to the pond's outlet (Fig. 2B).

QOP showed 2 different trends in palynofacies distribution within the 3 sediment samples analyzed. More than 50 % of sample 45-BE23-BE1 (#0 on Fig. 2C), located in the pond's delta, is rich in lignocellulosic fragments, coming from upper vegetation debris and terrestrial origin. Samples 45-BE23-BE2 (#1 on Fig. 2C) and 45-BE23-BE3 (#2 on Fig. 2C), located in the upstream part and in the main decantation basin of the pond respectively, are mainly composed of grey amorphous particles of algal origin, which is an authigenous production coming from the water column. Results also show that all samples contain newformed cubic pyrite (Fig. 2C).

3.1.2. Granulometric distribution

At the pond scale, and based on samples from 2021 (Fig. 3), fine sands are the most abundant granulometric fraction, with a mean content of 45.3 ± 6.7 % followed by coarse and fine silts, with their respective mean contents of 27.3 ± 3.1 % and 22.3 ± 4.2 %. Clays are reaching a mean value of 4.0 ± 0.5 % and coarse sands are the less abundant fraction at the pond scale, with a mean value of 1.2 ± 2.4 %.

Fine particles (clays + fine and coarse silts) are the most abundant fraction at the pond scale, with a mean content of 53.5 ± 7.6 %, and a maximum content of 65.2 %, reached in sample 45-BE21-BE12 #25, located nearby the main decantation basin of the pond (Table S2, Fig. 3A).

3.1.3. Crystalline phase analysis

XRD analysis of surface sediment samples from three distinct pond areas (for details see Fig. 3B) revealed slight variations in crystalline phases composition. The total crystalline phase content is constant in the 3 samples (from 36.7 to 37.7 %), with the dominants crystalline phase being quartz in sample 45-BE23-BE1 (#0) and kaolinite in samples 45-BE23-BE2 (#1) and 45-BE23-BE3 (#2) (Fig. S1, Table S3). Specific PDF (Powder Diffraction File) card numbers for each crystalline phase are provided in Texte S1. Identified crystalline phases are predominantly **silicates**, with **quartz and kaolinite** comprising more than 80 % of all crystalline phases, along with minor amounts of **sanidine and cristobalite** (Fig. 3B–Table S4). The silicate content varies by location, generally decreasing in decantation basin samples compared to delta samples, except for kaolinite. A similar trend is observed for zinc hydroxide (zinc oxide was used as internal standard for the quantification), which is associated with silicates. In contrast, **kaolinite and calcite** concentrations increase in the decantation basin. The **upstream area of the pond** has the highest **magnetite** content, whereas **sulfide (pyrite) concentrations decrease** across the sites. In bulk samples, pyrite is coated, and therefore protected by OM, meaning that as long as OM is not attacked, pyrite remains. During OM digestion, pyrite, also calcite, were exposed to the chemicals that might have oxidize them, causing them to disappear from the diffraction patterns (Fig. S2), while framboidal pyrite was also observed in QOC microscopy.

3.2. Pharmaceutical product distributions at the pond scale

ATE, TRA and MTP are the 3 cationic PPs quantified at the pond scale with median contents reaching 4.2, 10.1 and 8.8 ng/g respectively (Table S5). Spatially, their content distributions appear heterogeneous (Fig. 4A). Indeed, preferential accumulation occurred in the upstream part of the pond, and also in the downstream part, while the middle part exhibited lower contents.

Concerning neutral PPs, mean contents in CBZ, OXA, DIA and PAR are 64.0, 71.1, 34.1 and 1.5 ng/g respectively (Table S5). These neutral PPs contents also show spatial heterogeneity at the pond scale (Fig. 4B). One major hotspot is located in the delta. Cumulated neutral PPs contents are noteworthy higher than cumulated cationic PPs contents, reaching a difference of one order of magnitude. A Principal Component Analysis was performed in order to compare four PPs individual concentration spatial distributions. The four variables were CBZ, OXA, TRA and MTP concentrations, and the data set comprised the sampling campaigns of September 2021 and 2023. The first dimension, accounting for 47.2 % of the distribution, represents samples location at the pond scale, the delta samples being separated from the others. The second dimension, representing 33.2 % of the dispersion, represents the TOC content. It appeared that CBZ and OXA concentrations were decorrelated from TRA and MTP ones, highlighting also the existence of neutral and cationic PPs at the pond scale (Fig. S3).

4. Discussion

4.1. Bulk surface sediment compositions

The bulk composition of surface sediments samples between 2018 and 2022 allowed to determine TOC content and granulometric phase distributions at the pond scale. Results highlighted a TOC content gradient, increasing from upstream to downstream, and a preferential accumulation of FP in the main decantation basin of the pond. The characterization of 2023 surface sediments gave additionally the

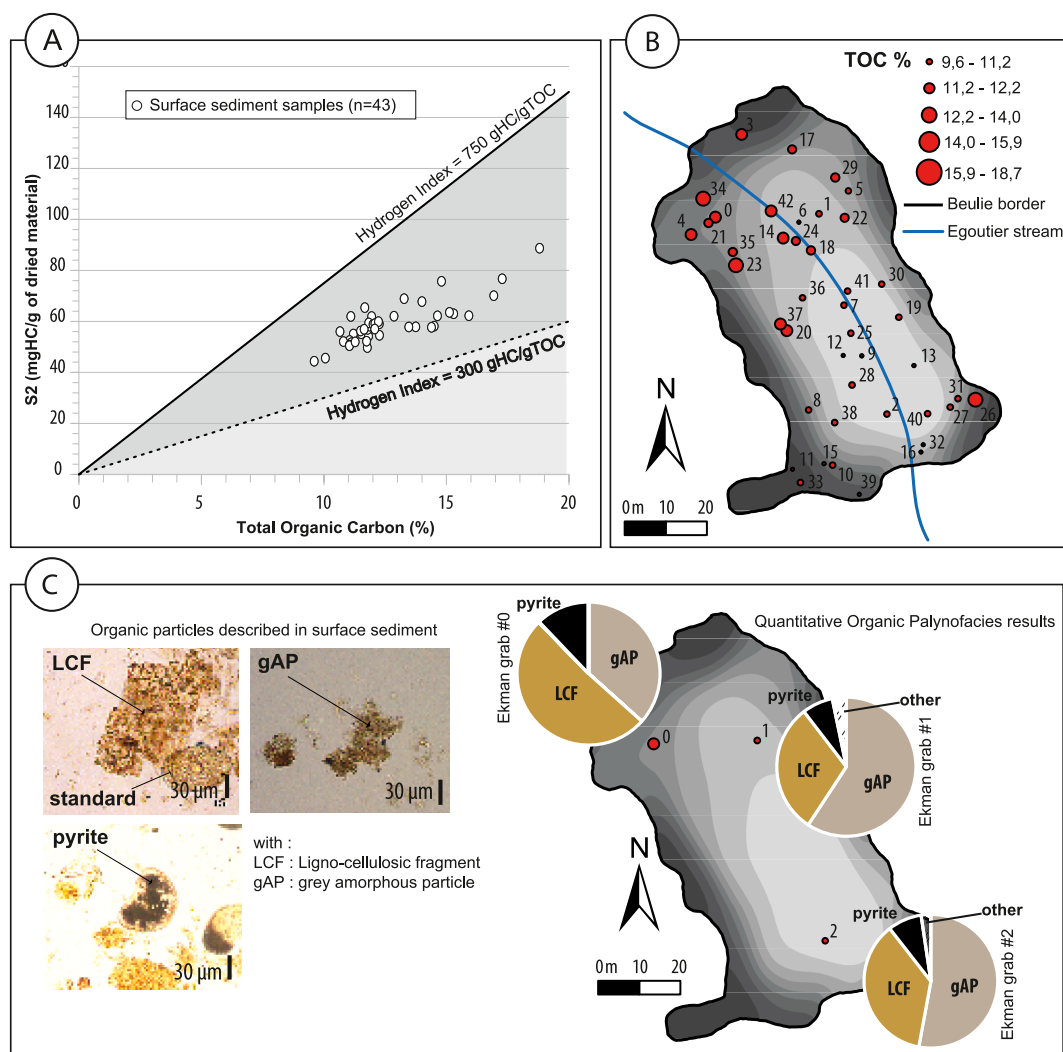


Fig. 2. S2 peak (mgHC/g of dried material) as a function of Total Organic Carbon (TOC, %), calculated for 43 surface sediments collected between September 2018 and September 2023 (A). Map representing the spatial distribution of TOC contents of sediment samples at the Beulie pond scale (B). Palynofacies quantified by QOP in the 3 sediment samples collected in September 2023, and their distribution within those sediment samples. The distribution corresponds to the mass of palynofacies over the total palynofacies mass (C).

crystalline inorganic phase distributions, and the organic palynofacies distributions, within 3 samples collected in the 3 selected areas: the delta #0, the upstream area of the pond #1, and the main decantation basin #2. The 3 samples have similar crystalline phase contents (37.2 ± 0.5 %). However, crystalline phase distributions are heterogeneous between the 3 samples, particularly regarding quartz and kaolinite, the 2 main phases. The kaolinite/quartz ratio is 0.32 in the delta, and reaches 1.51 and 1.55 in the upstream area and the main decantation basin, respectively. These two phases have very different properties, since quartz is not a phase susceptible to react with organic compounds such as PPs, while kaolinite has adsorptive properties. QOP results showed that OM heterogeneous spatial distribution is not only expressed with TOC contents, but also with variations in organic palynofacies distributions at the pond scale, with the delta accumulating preferentially OM with a terrestrial origin, and the upstream area and the main decantation basin accumulating preferentially algal OM (Fig. 5). QOP results also allowed to quantify newformed pyrite in surface sediments, supporting the occurrence of anoxic conditions within surface sediments. The extensive characterization of the 3 surface sediments enabled to isolate kaolinite from other less reactive inorganic sediment compartments, such as quartz. It also allowed to identify different OM typologies at the pond scale, being testament of either different OM sources or production

within the pond, which is a key information since all OM types don't have the same properties. This extensive characterization allowed to comprehend the differences in bulk sediment component into the pond, which is necessary to well apprehend the mechanisms behind bulk sediment component depositions and fate within the pond.

4.2. Mechanisms of sedimentation and organic matter dynamics in the pond

4.2.1. Sedimentation mechanisms

Surface sediments in the Beulie pond are the result of the decantation of a fraction of suspended particles transported by the Egoutier stream (Ledieu et al., 2021). The retention of suspended particles, such as FP, essentially depends on the residence time of the water in the pond: a balance between the inflow of water and the volume of the pond (Brune, 1953). Moreover, it also depends on the physical-chemical conditions within the water and the possible differences in signature between the tributary and the basin, particularly in terms of salinity and temperature (Mulder and Chapron, 2011). Measurements of superficial water temperature, carried out every year at the inlet and outlet of the pond, and within the Egoutier stream, highlighted a slightly higher water temperature in the stream upstream the pond than in the pond. Indeed, in

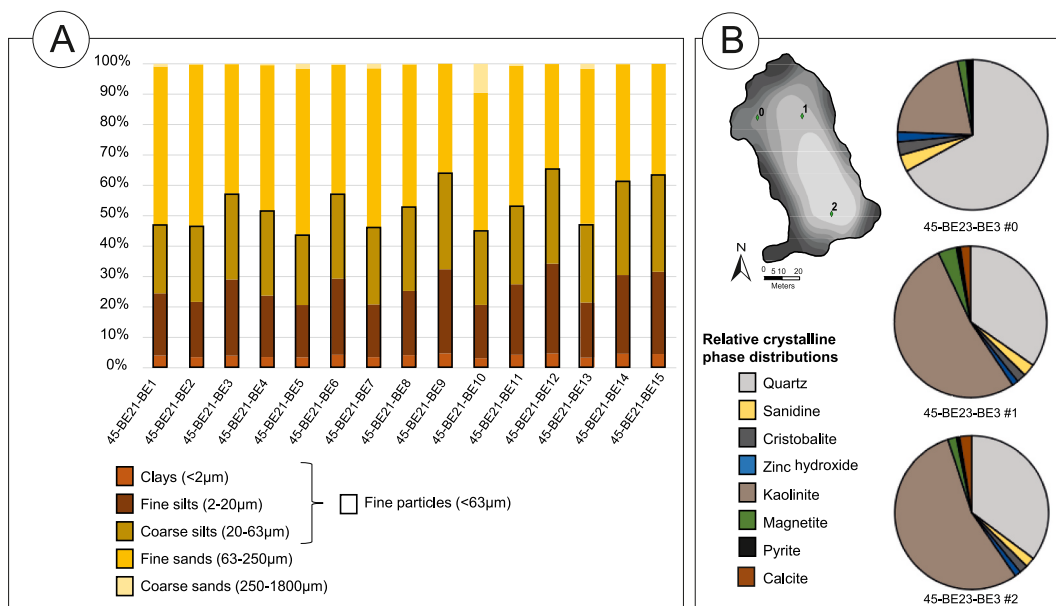


Fig. 3. Granulometric distribution given in % for the 15 samples collected in September 2021. (A). Relative crystalline phase distribution for the 3 bulk sediment samples collected in September 2023, including the composition in Quartz, Sanidine, Cristobalite, Zinc hydroxide, Kaolinite, Magnetite, Pyrite and Calcite (B).

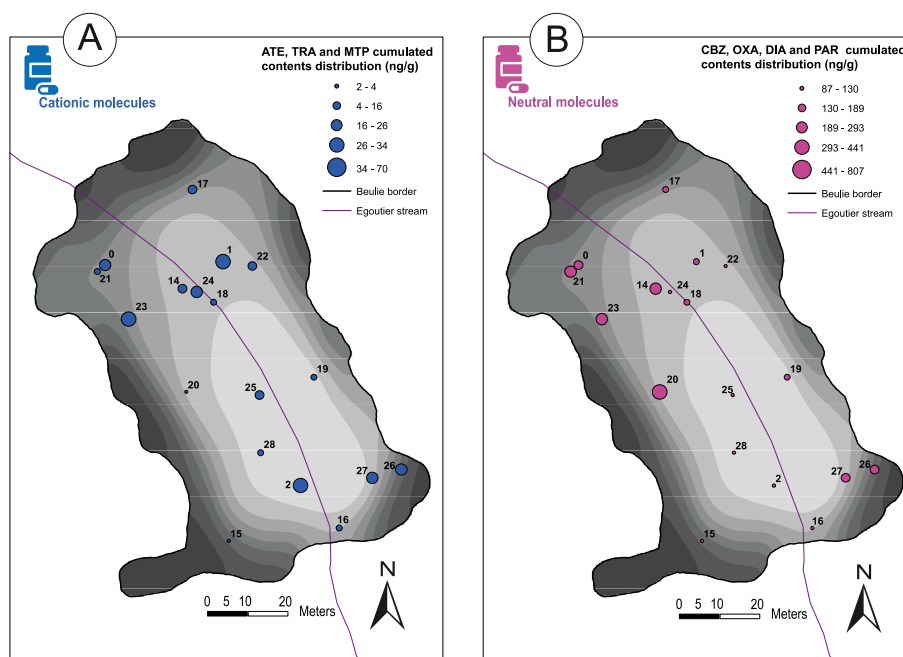


Fig. 4. Spatial distribution at pond scale of cumulated contents in cationic pharmaceutical products, including ATE, TRA and MTP (A). Spatial distribution at pond scale of cumulated concentration in neutral pharmaceutical products, including CBZ, OXA, DIA and PAR (B). Contents were quantified in 15 samples collected in September 2021 and 3 samples collected in September 2023.

September 2023, the stream water had a temperature of 17.4 °C, while the pond water had a temperature of 14.7 ± 0.9 °C (Fig. 6). Results are consistent with sedimentation mechanisms when hypopycnal flow occurs, when the tributary water has lower density than the pond water, coarser particles settle in the delta while finer particles settle in the basin. However, this trapping is uncompleted, and is highly dependent on the seasonal flow variations and extreme rainfall events. Indeed, PPs in suspended particulate matters were also quantified downstream the pond (Ledieu et al., 2021).

XRD measurements revealed that the basin contained more kaolinite than the delta, a known reactive component of FP (Miranda-Trevino and

Coles, 2003; Wang and Siu, 2006). TOC was mostly concentrated in the upstream part of the pond, especially in the delta. OM is known to play a role in particles flocculation in natural environments (Lee et al., 2017). This would explain its higher concentration close to the inlet of the pond, since when particles are flocculated with OM, their density increases, ending in their earlier sedimentation.

4.2.2. Organic matter dynamics in the pond

OM contents presented a heterogenous spatial distribution at the pond scale, with a preferential accumulation in the delta, as well as differences in its palynofacies composition, depending on surface

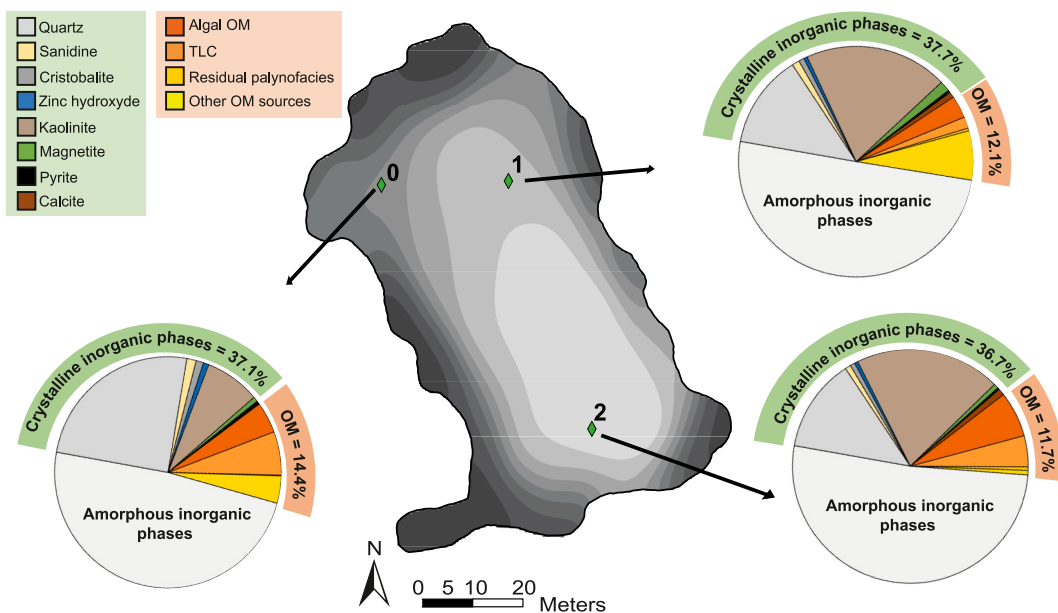


Fig. 5. Crystalline and organic compositions of surface sediment samples collected in September 2023 within the Beulie pond.

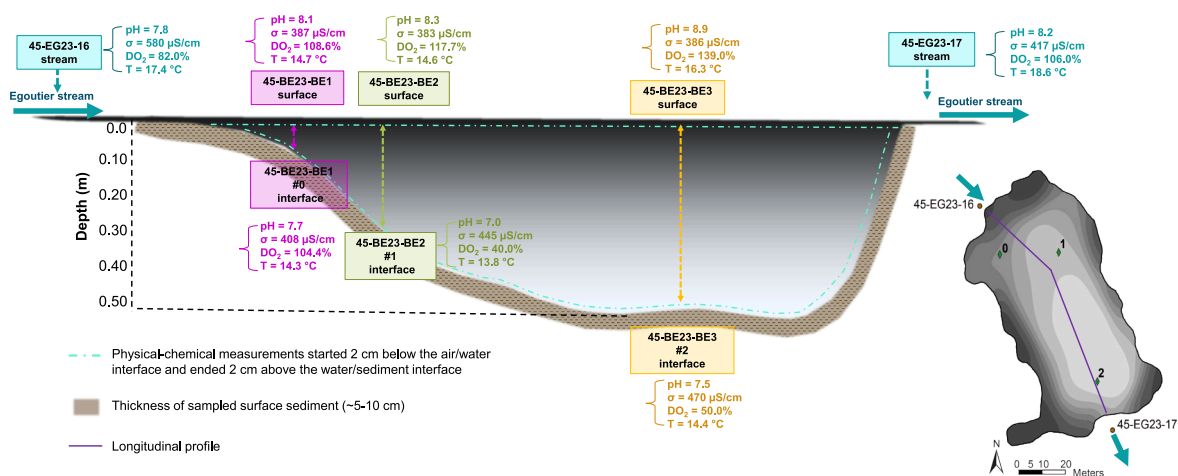


Fig. 6. Longitudinal profile performed from the delta to the main decantation basin of the Beulie pond. Physical-chemical measurement, including pH, electrical conductivity (σ), dissolved O_2 (DO_2) and temperature (T), were conducted in the stream at the pond's inlet (45-EG23-16), in the delta (45-BE23-BE1), out of the pond's channel (45-BE23-BE2), in the main decantation basin (45-BE23-BE3) and in the stream at the pond's outlet (45-EG23-16).

sediment location. OM in the delta was mostly from terrestrial origin, while OM in the basin was mostly from algal origin. Terrestrial OM finds mostly its source in the erosion of the watershed. When OM aggregates are transported by the stream, breakdown may occur favoring their mineralization (Doetterl et al., 2016). When OM aggregates reach the pond, the macroaggregates, denser and richer in organic carbon, will settle preferentially in the delta, while the smaller aggregates, less dense and poorer in organic carbon, will be more likely to settle in the main decantation basin of the pond. Furthermore, the higher proportion in algal OM in the main decantation basin might be explained by primary algal production.

In retention areas such as the Beulie pond, physical-chemical conditions may vary in the water-column, depending on profiles location at the pond scale. Indeed, in September 2023, while there was no relevant difference in the dissolved O_2 concentration between the water surface and the interface in the delta, significant decrease was observed for the dissolved O_2 concentration in the main basin, when reaching the interface. The delta is very shallow (Fig. 6), which might explain this

better oxygenation. Boye et al. (2017) proposed a connection between the thermodynamic preservation of OM in anoxic environments and the nominative oxidation state of carbon (NOSC), with a preferential degradation for sediments with higher NOSC, because of a lower energy cost. This means that variations of oxygenation conditions within the pond can generate differences in OM components degradation at the pond scale.

4.3. Pharmaceutical product trapping within surface sediments

4.3.1. Potential carrying phases of pharmaceutical product within surface sediments

Cationic and neutral PPs expose differences in terms of total average contents in surface sediments (1 order of magnitude). The 3 investigated cationic PPs, ATE, TRA and MTP have a moderate persistence in the aquatic environment, which might explain this difference of content. ATE had particularly low contents in sediments, which is consistent with its low $\log K_{ow}$ value, but also with its lower releasing rate through

WWTP effluents, compared with TRA (Ledieu et al., 2021). As surface sediments are mainly fed with SPM, lower interactions between PPs and SPM upstream the pond may also be responsible for their lower concentrations in surface sediments (Ledieu et al., 2021). The same observations can be made for PAR, the latter having in addition a low persistence (Table 1). Cationic and neutral PPs contents have similar spatial distributions at the pond scale in general, with hotspots based mainly in the delta and in the upstream area of the pond, as it is the case for TOC content spatial distribution. The same observation was made by Ledieu et al. (2021). However, samples with the highest content in total cationic PPs don't necessary reach the highest content in total neutral PPs. Cationic PPs also have a hotspot in the main decantation basin of the pond, as it is the case for kaolinite. Among the 3 areas sampled in 2023, the one located in the main basin exposed also the highest kaolinite content.

OM and kaolinite are known to be among the best sorbents for PPs (Aminot et al., 2015). Many studies have already highlighted PPs affinities for OM (Le Gaudu et al., 2022; Ke et al., 2023) and clays such as Kaolinite (Hounfodji et al., 2021). OM offers a variety of functional groups, for example carboxylic and phenolic ones, susceptible to create electrostatic interactions with cationic PPs. Concerning neutral PPs, the hydrophobic character of OM might be one of the main drivers of their adsorption (Park et al., 2018). Kaolinite can adsorb cationic PPs thanks to its cation exchange capacity, also neutral PPs thanks to its amphoteric edge-sites (Thiebault, 2020). However, the nature of adsorption mechanisms between kaolinite and PPs is not easily determined by experimental studies. Hounfodji et al. (2021) proposed an atomistic simulation approach, highlighting hydrogen bond interactions between PPs functional groups, such as hydroxyl group, and the aluminol surface of kaolinite.

4.3.2. Environmental drivers of PPs fate in pond systems

PPs trapping within the Beulie pond is only partial, since they are still quantified in SPM downstream the Beulie pond (Ledieu et al., 2021). Furthermore, the fraction of trapped PPs, adsorb onto SPM, is variable, on relies on hydrology events, and resulting sedimentation mechanisms. Some studies conducted in similar context (pond) suggests to particularly investigate horizontal current patterns, likely to vary following the hydrologic regime (Schimmelpfennig et al., 2016). Even if PPs content trends at the pond scale remain, they might not be systematical, resulting in this uncomplete trapping.

The longevity of PPs adsorption onto settled SPM components, especially OM and kaolinite, is also questionable. Indeed, OM and kaolinite states are highly dependent on dissolved O₂ and pH conditions respectively, the charges of kaolinite adsorption sites depending on the pH (Li et al., 2010), and these conditions are heterogeneous at the pond scale (Fig. 6). Other studies also observed a dependence of water-column oxygenation based on the temperature, with preferential aerobic conditions in winter (Massmann et al., 2006). This suggests that seasonal variations, affecting the state, or the preservation of kaolinite and OM might result in PPs desorption from their carrying phases. In general, a factor rarely studied in the literature is sediment diagenesis in the natural environment (Klaminder et al., 2015), and more precisely the influence that sediment oxidation or reduction may have on sorbed PPs. Furthermore, PPs characteristics are also concerning for their fate in retention areas. Indeed, some PPs are known to be redox-dependent (Maeng et al., 2011), which make them sensitive to water-column oxygenation changes. In general, PPs fate is also highly dependent on their polarity (Thiebault, 2020), which relies on pH variations. This supports the importance of considering the water-column and the water-sediment interface physical-chemical characteristics, since they remain necessary to understand PPs fate and spatial distribution at the pond scale.

5. Conclusions

This work studied the spatial distributions of bulk matrix components (particularly FP and TOC), and of cationic (ATE, TRA and MTP) and neutral (CBZ, OXA, DIA and PAR) PPs, which were quantified in surface sediments collected within the Beulie pond (Egoutier, France). The study allowed to (i) identify spatial heterogeneity at the pond scale of both the bulk matrix components PPs contents and (ii) identify preferential accumulation of bulk matrix components and concentration of PPs areas. Results allowed to make the connection between the granulometric distribution of particles at the pond scale and classic settling mechanisms, and also supports the preferential accumulation of TOC in the delta of the pond. These observations suggest that looking for PPs carrying phases in surface sediment in a retention area requires to gauge the spatial distribution of sediment components. Moreover, these components shall be not only evaluated in terms of content, but also in terms of typology and state (degradation, reactivity, charge). This suggest to study commonly the particulate phase, embedded by surface sediment, and the overlying aqueous phase, in our case the water-column and its physical-chemical characteristics.

This work allowed to (i) identify preferential accumulation and concentration areas within the pond even though a seasonal variability of SPM decantation may occur, and to (ii) highlight the necessity to proceed in a two steps approach, with firstly a high resolution characterization of the surface sediments, followed by a selection of areas, representative of specific accumulation and concentration behaviors, in order to proceed a finer characterization of sediment components, including their content, state, and reactivity under specific physical-chemical conditions.

CRedit authorship contribution statement

Amélie Humbrecht: Methodology, Data curation, Validation, Formal analysis, Conceptualization, Writing – original draft, Investigation. **Anaëlle Simonneau:** Validation, Project administration, Funding acquisition, Conceptualization, Writing – original draft, Resources, Methodology, Formal analysis, Visualization, Supervision, Data curation. **Thomas Thiebault:** Writing – review & editing, Validation, Formal analysis, Visualization, Methodology, Data curation. **Gauthier Bernier-Turpin:** Visualization, Formal analysis, Validation, Data curation, Writing – review & editing, Methodology. **Claude Le Milbeau:** Validation, Data curation, Visualization, Formal analysis, Writing – review & editing, Methodology. **Veronika Veselská:** Visualization, Funding acquisition, Data curation, Validation, Formal analysis, Writing – review & editing, Methodology. **Josef Kašlík:** Writing – review & editing, Validation, Formal analysis, Methodology, Data curation, Visualization. **Gildas Ratié:** Visualization, Writing – review & editing, Validation, Funding acquisition. **Lauriane Ledieu:** Writing – review & editing, Visualization, Validation. **Lydie Le Forestier:** Validation, Writing – review & editing, Supervision.

Declaration of competing interest

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

Acknowledgments

The authors thank the anonymous reviewers for their constructive comments and suggestions. This research was funded by the Region Center-Val-de-Loire (France) and is part of the TRANSAT Project led by A. Simonneau (contract 2020–00138873) and supported by the Barande Mobility Project 2022–2023 and Labex VOLTAIRE, France (10-LABX-0100). V. Veselská acknowledges the support of the ERDF/ESF project TECHSCALE (No. CZ.02.01.01/00/22_008/0004587). The

authors acknowledge the assistance provided by the Research Infrastructure NanoEnviCz, supported by the Ministry of Education, Youth and Sports of the Czech Republic under Project No. LM2023066. The authors are grateful to the members of GEOMIN platform of ISTO for their help, the analytical and technical support, and more particularly to N. Freslon, R. Boscardin and M. Hatton, and also to A. Jouannetaud for QOP analysis. The authors also acknowledge the staff of the METIS analytical platform for LC-MS analysis, in particular F. Alliot, and are also grateful to ISTEP for laser-granulometry measurements, in particular to L. Le Callonnet.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2025.106487>.

Data availability

The data supporting this study are available in the [recherche.data.gouv](https://recherche.data.gouv.fr) repository.

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