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a combined field and laboratory approach in a suburban context

Comportement des produits pharmaceutiques dans le continuum eau-sédiments :
une approche couplée terrain-laboratoire en contexte péri-urbain

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List of abbreviations

AT = anthropogenic tracers

DOC = dissolved organic carbon

Eh = redox potential

FPs = fine particles

FTIR = Fourier-transformed infrared

HDPE = high density polyethylene

HI = hydrogen index

HVLP = high volume low pressure

LC-MS/MS = liquid chromatography coupled with tandem mass spectrometer

LOD = limit of detection

LOQ = limit of quantification

NOSC = nominative oxidation state of carbon

OC = organic carbon

OM = organic matter

PPs = pharmaceutical products

PTFE = poly-tetrafluoroethylene

SPE = solid-phase extraction

QOP = quantitative organic petrography

SPMs = suspended particulate matter

TEA = terminal electron acceptor

TED = terminal electron donor

TOC = total organic carbon

WWTPs = wastewater treatment plants

Résumé étendu

Introduction générale

Dans un contexte de pressions anthropiques croissantes, l'étude des transferts de masse et d'énergie œuvrant au sein de la zone critique (ZC) devient indispensable à la bonne compréhension des cycles biogéochimiques existant entre les différents compartiments, incluant l'atmosphère, l'hydrosphère, la biosphère, la pédosphère et la lithosphère (Anderson et al., 2004 ; Gaillardet et al., 2018). Ces cycles ont été étudiés presque exclusivement pour la phase dissoute. La prise en compte de la phase particulaire (flux particulaires = matières en suspension dans les cours d'eau, sédiments) est pourtant indispensable à l'élaboration de bilans de masse précis dans le cycle d'éléments tels que le carbone, dont elle représente une contribution importante (Manninen et al., 2023). Pour ce faire, les bassins-versants ont été progressivement instrumentés afin de suivre les paramètres hydrologiques, géomorphologiques, géologiques et géochimiques, susceptibles d'influencer le transfert des éléments dans le continuum dissous-particulaire. Ceci s'est traduit notamment par le développement de services nationaux d'observation (Pierret et al., 2018 ; Gogo et al., 2021).

Parallèlement à l'artificialisation des sols qui augmente leur vulnérabilité face aux événements tels que les précipitations extrêmes, et également la charge particulaire des cours d'eau, une nouvelle forme de pression anthropique a fait suite à l'urbanisation croissante des bassins-versants, certains par la suite qualifiés de bassins-versants « péri-urbains » : l'émission de traceurs d'origine anthropique (Pascual-Aguilar et al., 2015). Ils désignent entre autres les métaux lourds (Murray et al., 2004), les pesticides, et les microplastiques (Dris et al., 2015), et sont émis dans l'environnement via différentes entrées tels que les pratiques agricoles, les activités industrielles et les effluents des stations d'épuration (Jacob et al., 2020 ; Pérez et al., 2021 ; Qin et al., 2022). L'affinité reconnue des traceurs anthropiques pour la phase particulaire a conduit à leur étude dans le continuum dissous-particulaire indispensable à la bonne compréhension de leur transfert et de leur devenir dans l'environnement. Les dernières décennies ont également été marquées par une vigilance accrue portée sur les polluants organiques persistants (POPs), incluant notamment les substances hydrocarbures aromatiques polycycliques. De plus, la Convention de Stockholm a également publié un rapport indiquant la nécessité d'étudier le comportement de nouveaux POPs dans l'environnement, à l'instar des produits pharmaceutiques (PPs, Mbengue, 2001).

La seconde moitié du 20^{ème} siècle a été témoin de nombreux progrès dans le domaine de la pharmacologie (Académie nationale de Pharmacie, 2019). Il existe aujourd'hui plus de 3000 PP, des molécules conçues pour être efficaces y compris à faible concentration (Hernando et al., 2006). Cependant, une fois excrétées par le corps humain et émises dans l'environnement, notamment via les effluents des stations d'épuration, certaines de ces molécules demeurent actives, voire même toxiques pour les espèces aquatiques (Paiga et al., 2016). Leur hydrophilie explique une bibliographie principalement centrée sur la phase dissoute, mais plusieurs articles ont cependant démontré que les PP s'adsorbaient également sur la phase particulaire, alors déterminante dans leur transfert à l'échelle des bassins-versants, intégrant de larges surfaces urbaines ($>100 \text{ km}^2$), mais aussi à plus petite échelle ($5\text{-}10 \text{ km}^2$, Thiebault et al., 2021 ; Ledieu et al., 2021). Ces « petits » hydrosystèmes sont en effet reconnus comme étant plus sensibles et ayant une réponse hydrologique plus rapide aux pluies intenses (i.e. crues éclair). Il existe cependant encore peu d'études ayant déterminé les matrices réactives du continuum dissous-particulaire susceptibles d'adsorber les PP, ainsi que les paramètres capables d'influencer la stabilité/réversibilité de leur piégeage sur la matrice particulaire, questionnant alors directement leur mobilité et leur persistance dans l'environnement.

Principaux objectifs de la thèse :

Ce travail de thèse fait partie du projet TRANSAT (Transfert particulaire des contaminants en bassin versant anthropisés), financé par la Région Centre-Val-de-Loire et porté par Anaëlle Simonneau. Le projet a pour objectif d'étudier le comportement de contaminants émergents, les produits pharmaceutiques (PP), dans le continuum eau-sédiment à l'échelle du bassin-versant. Le bassin-versant de l'Egoutier (Semoy, Loiret, France), hébergeant le site instrumenté OBSCURE et faisant partie du SNO Observil, a été suivi dans ce but. Le travail de thèse s'intéresse plus particulièrement à l'étang de la Beulie, une zone de rétention péri-urbaine sur le bassin-versant de l'Egoutier, située en aval de deux rejets d'effluents de stations d'épuration, et dont les processus physico-chimiques intrinsèques pourraient influencer l'adsorption et la spéciation des PP. Ce travail de thèse a ainsi pour but d'identifier et de discuter les interactions entre les PP et les matrices réactives du continuum eau-sédiment, susceptibles de les adsorber ou de les complexer.

Les principaux objectifs sont :

- 1) Déterminer les processus à l'origine de la distribution spatiale des matrices composant les sédiments d'interface et des PPs à l'échelle de l'étang de la Beulie
- 2) Identifier les potentielles phases porteuses des PPs au sein du continuum eau-sédiment, et déterminer les facteurs responsables d'une telle affinité.
- 3) Comprendre les mécanismes d'adsorption/désorption se produisant entre les PPs et leurs phases porteuses.
- 4) Explorer le rôle des paramètres physico-chimiques, en particulier le pH, le potentiel redox, la conductivité électrique et l'oxygène dissous, dans la diagenèse de la matière organique sédimentaire et, en conséquence, dans la stabilité et la réversibilité du piégeage des PPs au sein des sédiments d'interface.

La démarche scientifique repose sur une approche couplée terrain-laboratoire, incluant un échantillonnage à haute résolution spatiale de l'interface eau/sédiment de l'étang de la Beulie, la caractérisation physico-chimique saisonnière de la colonne d'eau depuis la surface jusqu'à l'interface eau/sédiment, la caractérisation géochimique des matrices particulières et aqueuses à l'échelle de l'étang, et enfin l'élaboration d'expériences d'adsorption en batchs entre les matrices composants les sédiments d'interface et des solutions de PPs « pures ».

Organisation du manuscrit :

Le manuscrit est organisé en 5 chapitres :

Le Chapitre 1 décrit les sources, la composition et la réactivité géochimique des principales matrices présentes dans les masses d'eau, et susceptibles d'interagir avec les PPs, en contexte péri-urbain. Il présente également la chronologie des études menées sur la présence et le devenir des PPs dans le milieu naturel, et explicite les raisons justifiant ce type d'études dans des bassins-versants de plus petite échelle.

Le Chapitre 2 présente les stratégies d'échantillonnage, analytiques et expérimentales choisies, ainsi que la pertinence de l'étang de la Beulie comme zone d'étude.

Le Chapitre 3 explore la distribution spatiale, à l'échelle de l'étang de la Beulie, des teneurs des différentes matrices composant les sédiments d'interface, telles que la matière organique et les argiles, ainsi que celle des teneurs en PPs. Il discute par ailleurs l'effet de la composition et de l'accumulation des sédiments sur la distribution spatiale des PPs. Ce travail a été publié sous la forme d'un article dans la revue *Applied Geochemistry* en 2025 : *Humbrecht, A., Simonneau, A., Thiebault, T., Bernier-Turpin, G., Le Milbeau, C., Veselská, V., ... & Le Forestier,*

L. (2025). *Effect of sediment composition and accumulation on pharmaceutical product spatial distributions at the suburban pond scale (Beulie pond, SNO Observil, France)*. *Applied Geochemistry*, 190(10648), 7.

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Le Chapitre 4 étudie les propriétés de la matière organique sédimentaire, telles que sa composition en groupes fonctionnels et sa réactivité, susceptibles d'expliquer son affinité pour les PP. Ce travail a été rédigé sous la forme d'un article pour soumission dans la revue *Environmental Research*.

Le Chapitre 5 explore la stabilité du piégeage des PP sur la matrice sédimentaire, ainsi que les facteurs pouvant contrôler les processus d'adsorption et de désorption. Il propose ainsi une approche expérimentale préliminaire, étudiant les cinétiques et les mécanismes d'adsorption/désorption de deux PP, la carbamazépine et le tramadol.

Chapitre 1 : Etat de l'art des origines, formes et devenir des matrices naturelles et réactives et des produits pharmaceutiques dans les masses d'eau en contexte péri-urbain.

Le Chapitre 1 réalise un état de l'art des matrices environnementales présentes dans les masses d'eau, sous forme particulaire ou dissoute, et qui constitue un intérêt dans l'étude du devenir de polluants émergents tels que les PP dans l'environnement. Il présente également une chronologie des études réalisées plus particulièrement sur les PP, qu'elles portent sur leur présence dans l'environnement ou leur devenir.

La MO fait partie des matrices particulièrement étudiées dans les masses d'eau (Sharp et al., 2006 ; Bhatnagar and Sillanpää, 2017). Elle peut avoir une origine allochtone ou autochtone, qui désignent respectivement une contribution du bassin versant par humification puis érosion des sols, ou une contribution de la décomposition des plantes ou de la production primaire algale (Beckett and Ranville, 2006). Dans les environnements périurbains, la MO peut également avoir une origine anthropique, provenant bien souvent des effluents des stations d'épuration (STEPs, Zheng et al., 2024). La MO a une structure complexe, que l'on qualifie en général d'associations supramoléculaires, composées de longues chaînes carbonées (Sposito, 2008). Elle peut être fractionnée selon sa solubilité en milieu acide ou basique, et l'on distingue particulièrement les acides humiques, solubles en milieu basique, les acides fulviques, solubles quel que soit le pH, et l'humine, insoluble (Stevenson, 1994). La MO contient un grand nombre de groupes fonctionnels, tels que les carboxyles, les phénols, les carbonyles et les quinones (Hayes and Swift, 1978). Dans l'environnement, la MO est soumise à la diagénèse précoce, phénomène qui tient compte de paramètres physico-chimiques tels que le pH et le potentiel d'oxydoréduction (Tardy, 1997 ; Boye et al., 2017). Les microorganismes participent largement à sa décomposition, suivant ces mêmes conditions. Ses groupes fonctionnels lui conférant la capacité de créer des liaisons de type électrostatiques ou hydrophobes, la MO est aussi très étudiée pour son affinité avec des traceurs d'origine anthropique tels que les métaux lourds, mais aussi des molécules organiques tels que les PP (Maoz and Chefetz, 2010).

Dans le continuum eau-sédiment, on retrouve aussi des matrices minérales, tels que les oxydes et les minéraux argileux, également susceptibles de porter des traceurs d'origine anthropique (Han et al., 2019 ; Zhao et al., 2017). Les minéraux argileux sont des phases porteuses particulièrement intéressantes d'une part pour leur grande surface spécifique et d'autre part pour la stabilité et la durabilité des liaisons qu'ils créent (Ewis et al., 2022). Le

groupe des kaolinites représente le groupe le plus abondant des minéraux argileux dans les sols (Sposito, 2008), et a fait l'objet de beaucoup d'études pour sa capacité à porter des traceurs d'origines anthropiques tels que les métaux traces ou les produits pharmaceutiques.

Parmi les progrès ayant marqué la seconde moitié du 20^{ème} siècle, les innovations en médecine et en pharmacologie ainsi que la consommation de produits pharmaceutiques peuvent être considérés comme des marqueurs de pays développés. Aujourd'hui, plus de 3000 molécules pharmaceutiques actives existent (Académie nationale de Pharmacie, 2019). Leur principe actif est capable d'agir sur l'organisme même à faible concentration. Cependant, le corps humain ne les métabolise pas entièrement, si bien qu'ils sont, une fois excrétés, quantifiables dans l'environnement. Les produits pharmaceutiques (PPs) sont différenciables par leur composition chimique et leur classe thérapeutique, mais aussi par leur persistance dans l'environnement et leurs propriétés physico-chimiques. Les progrès réalisés en chimie analytique quantitative, tels que le développement de la chromatographie liquide couplée à des spectres de masse en tandem (LC-MS/MS) ont permis de les quantifier dans l'environnement, en phase solide comme dissoute, à des teneurs avoisinant respectivement le ng/g ou ng/L. L'enjeu repose également sur la toxicité des PPs, effective même à ces faibles concentrations, sur les organismes vivants, à l'image de certaines espèces de poissons menacées par les hormones, ou des communautés bactériennes par les antibiotiques. Leur consommation à l'échelle mondiale varie d'un pays à l'autre, en fonction notamment de l'accès aux soins médicaux, et leur présence dans l'environnement, le plus souvent attribuable aux effluents des stations d'épuration, dépend également de la qualité du traitement des eaux usées (Wilkinson et al., 2022). Leur devenir dans l'environnement dépend de leur propriété, certaines molécules étant facilement photodégradables, comme le paracétamol, tandis que d'autres, telles que la carbamazépine, affichent une persistance élevée. Leur transfert dans le continuum eau-sédiment repose sur leur affinité avec notamment les matières en suspension (MES, Boulard et al., 2020)), sur leurs propriétés intrinsèques telles que leur charge, mais également sur la dégradation de la matrice particulaire dans l'environnement. Cette étude s'intéressera particulièrement au cas du tramadol (TRA), de l'aténolol (ATE), de la fluoxétine (FLX), de la venlafaxine (VFX), du métoprolol (MTP), de la carbamazépine (CBZ), du diazépam (DIA), de l'oxazépam (OXA), du paracétamol (PAR) et du diclofenac (DIC).

Le devenir des PPs dans l'environnement a souvent été abordé dans des études s'intéressant à de larges surfaces drainées, sur des bassins versants d'une superficie généralement supérieure à 100 km². Cependant, des études plus récentes, menées sur des

bassins versants à plus petite échelle ($< 5\text{-}10 \text{ km}^2$) ont démontré leur sensibilité plus importante à la pression anthropique, et ont également montré que les teneurs moyennes en PPs quantifiées dans les différents compartiments (effluents de STEPs, eau de cours d'eau, MES, sédiments accumulés dans des zones de rétention) pouvaient atteindre le même ordre de grandeur que sur des bassins versants à plus grande échelle (Thiebault et al., 2021 ; Ledieu et al., 2021).

Chapitre 2 : Présentation du site d'étude, de l'approche scientifique et des stratégies analytiques et expérimentales

Le chapitre 2 présente la stratégie mise en œuvre, du terrain au laboratoire, pour identifier le comportement des PPs dans le continuum eau-sédiment. Ce chapitre montre en particulier la pertinence de l'étang de la Beulie comme zone d'étude, et décrit l'ensemble des analyses effectuées sur les sédiments d'interface et l'eau de l'étang afin de déterminer les matrices réactives susceptibles de porter les PPs, ainsi que les facteurs pouvant influencer cette affinité. Il présente enfin les expériences mises en œuvre afin de déterminer les mécanismes d'adsorption et leur stabilité/réversibilité.

Les études portant sur la présence de PPs dans les matrices particulières et aqueuses explorent rarement l'influence de paramètres tels que l'hydrologie, la géochimie et la géomorphologie des bassins-versants. Pourtant, lorsque les PPs sont émis dans l'environnement par le biais des effluents des stations d'épuration (STEPs), comme souvent le cas (*cf* Chapitre 1), leur concentration dans le milieu naturel va dépendre du débit de la masse d'eau réceptrice, tandis que leur forme et leur charge vont dépendre de conditions telles que le pH en relation avec leur valeur de leur constante d'équilibre (pK_a). De plus, leur devenir va dépendre des phases porteuses présentes, dont la géochimie va influencer leur affinité pour les PPs. Enfin, la connectivité du bassin-versant et sa topographie vont en partie déterminer la distance de transfert des PPs. En effet, lorsque les cours d'eau sont interrompus ou s'achèvent dans des zones de rétention, telles que les étangs ou les lacs, leur charge particulière, susceptible de contenir des PPs, s'accumule par effet de sédimentation, ce qui limite ainsi la distance parcourue des PPs dans l'environnement. De plus, les bassins-versants à grande échelle ($>100 \text{ km}^2$) sont souvent privilégiés dans les études, car ils intègrent davantage de volumes d'effluents et donc une population équivalente plus importante. Pourtant, des études récentes ont montré que les bassins-versants à plus petite échelle ($5\text{-}10 \text{ km}^2$) étaient tout à fait pertinents pour ce type d'étude, car ils montrent souvent une réponse plus rapide aux événements hydrologiques extrêmes et une sensibilité plus accrue à ce type

de pollution (cf Chapitre 1). Les méthodes d'échantillonnage et les stratégies analytiques sont également variables d'une étude à l'autre. Les échantillonnages à haute résolution temporelle sont souvent privilégiés au détriment de la résolution spatiale, pourtant nécessaire à la prise en compte de l'hétérogénéité du milieu naturel (Larà-Martin et al., 2015). De plus, la caractérisation des phases porteuses, essentielle à la compréhension de leur affinité pour les PPs, est souvent limité à des paramètres généraux tels que la composition en argiles et la teneur en carbone organique total (COT). Enfin, les approches expérimentales visant à déterminer les mécanismes et cinétiques d'adsorption sont souvent menées indépendamment des études de terrain, ce qui ne permet pas de faire le lien entre d'une part les conditions physico-chimiques du milieu naturel, et d'autre part la géochimie des phases porteuses associées aux processus d'adsorption mis en évidence en laboratoire.

Ce travail propose ainsi de coupler un échantillonnage à haute résolution spatiale avec une caractérisation fine des matrices dissoutes et particulières, complétés par une approche expérimentale en batch visant à identifier les mécanismes et les cinétiques du comportement des PPs dans le continuum eau-sédiment, au regard des conditions physico-chimiques du milieu naturel et des propriétés des matrices susceptibles de les porter, en termes de composition, typologie et propriétés réactives. Il s'inscrit dans le cadre du projet TRANSAT (« Transfert particulaire des contaminants en bassin versant anthropisé »), financé par la Région Centre-Val-de-Loire et piloté par Anaëlle Simonneau, et qui propose d'étudier le comportement de contaminants émergents tels que les PPs dans le continuum eau-sédiment à l'échelle d'un bassin versant périurbain.

Le site d'étude choisi est le bassin versant de l'Egoutier, situé au nord-est d'Orléans, d'une surface étudiée de 6,9 km² et caractérisé par un gradient de pression anthropique croissant d'amont en aval. La présente étude est focalisée principalement sur l'étang de la Beulie, qui est une zone de rétention d'environ 4000 m² située en aval de deux rejets d'eaux usées, respectivement de la Pharmacie Générale des Armées et d'un hôpital psychiatrique. Un précédent travail a permis de mettre en évidence les teneurs importantes en PPs issus de ces effluents, ainsi que leur présence non négligeable dans la phase particulaire (Ledieu, 2020 ; Ledieu et al., 2021). Les données acquises sur les matrices dissoutes et particulières entre 2018 et 2024 ont permis de montrer, d'une part la réponse hydrodynamique rapide du bassin versant face aux événements tels que les crues, et, d'autre part de montrer le rôle joué par l'étang de la Beulie dans l'accumulation de particules, et également des PPs adsorbés sur cette matrice particulaire. Ces données ont également permis de mettre en évidence les contrastes

géochimiques, notamment en termes de pH et de concentration et qualité de la matière organique, entre le linéaire du cours d'eau et l'étang de la Beulie, suggérant des contraintes environnementales particulières dans les zones d'accumulation de la matrice particulaire et des PPs.

Stratégie d'échantillonnage :

Un échantillonnage à haute résolution spatiale a été réalisé dans l'étang de la Beulie, afin de collecter le sédiment à l'interface eau/sédiment, constituant la phase particulaire. De plus, la phase aqueuse a également été échantillonnée à l'interface eau/sédiment, afin de caractériser le comportement des PPs dans ce continuum. Les matières en suspension, transportées par le cours d'eau et à l'origine des sédiments d'interface de la Beulie, ont également été collectées et caractérisées dans le cadre du projet TRANSAT, mais ne font pas partie intégrante de la thèse qui s'intéresse au comportement des PPs dans le contexte particulier offert par l'étang de la Beulie, notamment en termes de diagénèse précoce du sédiment.

Stratégie analytique :

La stratégie analytique propose de caractériser finement les matrices du continuum eau-sédiment susceptibles de porter les PPs. L'intérêt se porte en particulier sur la MO et les phases minérales telles que les argiles, dont les affinités pour les PPs ont déjà été décrites dans plusieurs études. La MO a été quantifiée par mesure du COT (%), grâce à la pyrolyse Rock-Eval, dont le paramètre S2 (potentiel de génération d'hydrocarbures (HC), exprimé en mgHC/gCOT) a permis de déterminer son degré de maturité. La composition élémentaire de la MO a été déterminée par pyrolyse FLASH, permettant d'obtenir la distribution molaire en carbone, hydrogène, azote, soufre et également oxygène par soustraction. Sa typologie a été étudiée par l'analyse quantitative des palynofaciès, qui permet notamment de différencier la MO d'origine algale de la MO d'origine terrigène. Enfin, ses principaux groupes fonctionnels ont été déterminés par spectroscopie infrarouge à transformée de Fourier (FTIR). Les argiles et les oxydes ont été quantifiés par diffraction des rayons X. Les PPs ont également été quantifiés dans les matrices dissoutes et particulaires par LC-MS/MS.

Stratégie expérimentale :

La stratégie expérimentale propose de déterminer les facteurs influençant la stabilité du piégeage des PPs par les sédiments d'interface de la Beulie et de déterminer la potentielle synergie existante entre les matrices du sédiment, notamment la MO et les argiles.

Pour ce faire, des profils physico-chimiques incluant les mesures du pH, de la conductivité électrique, du potentiel d'oxydoréduction (Eh), de l'oxygène dissous et de la température, ont été réalisés depuis la surface jusqu'à l'interface eau-sédiment de l'étang de la Beulie.

Les sédiments ont subi un tamisage humide réalisé avec de l'eau ultra-pure ou de l'eau de l'étang, afin d'en isoler 5 fractions granulométriques : >1 mm ; 250 μ m-1 mm ; 160 μ m-250 μ m ; 63 μ m-160 μ m et <63 μ m. L'eau de tamisage a été récupérée par centrifugation de la fraction <63 μ m afin de quantifier des concentrations éventuelles de carbone organique dissous (COD) et de PPs. La MO a été caractérisée dans les différentes fractions granulométriques du sédiment, chacune illustrant des tailles et des densités de particules différentes, et donc des vitesses de sédimentation et potentiellement des états de dégradation différents. La diagénèse précoce de la MO pouvant impacter sa fonctionnalisation et donc sa capacité à créer des liaisons avec les PPs, ses propriétés réactives dans les différentes fractions granulométriques du sédiment ont été calculées à partir de sa composition élémentaire. Cette composition élémentaire a en effet permis de calculer l'état nominal d'oxydation du carbone, puis son énergie libre de Gibbs dans l'état standard, permettant de calculer son activité en fonction du potentiel d'oxydoréduction. Enfin, les PPs ont été quantifiés dans les deux classes granulométriques extrêmes (>1 mm et <63 μ m) en plus de la matrice globale.

Afin d'identifier les cinétiques d'adsorption/désorption des PPs sur la matrice particulaire, une expérience de cinétique a été réalisée, mettant en interaction du sédiment d'interface de la Beulie avec de l'eau de la colonne d'eau, collectée à l'interface eau-sédiment. Des prélèvements de la phase dissoute ont été réalisés à intervalles de temps réguliers au cours de l'agitation du sédiment avec l'eau de l'étang afin de quantifier les PPs par analyse LC-MS/MS, et d'en déduire d'éventuels échanges entre la phase dissoute et la phase particulaire. A chaque prélèvement, le pH, le potentiel d'oxydo-réduction (Eh), la conductivité électrique et l'oxygène dissous étaient également mesurés.

Enfin, des expériences en batch ont été réalisées dans le but d'évaluer la capacité d'adsorption du sédiment d'interface de la Beulie comparativement à une matrice « pure », ici la kaolinite KGa-2. La phase solide était constituée du sédiment d'interface, ou de la kaolinite pure, ou un mélange des deux phases, tandis que la phase dissoute était constituée d'une solution de molécules pharmaceutiques « pures », ici la carbamazépine ou le tramadol respectivement. Ces deux PPs ont été sélectionnés car ils ont une charge différente, la carbamazépine étant neutre et le tramadol chargé positivement dans les conditions

environnementales de la Beulie (pH entre 6 et 8). Les concentrations initiales en PPs (10-20 mg/L) sont plus élevées que celles du milieu naturel, et les phases dissoutes ont été préparées avec un fond ionique de CaCl_2 0,01 M, généralement utilisé pour sa composition proche de celle des eaux de surface, et qui est également cohérente avec la composition chimique de l'eau de la Beulie, sans incidence du carbone organique dissous. L'expérience a été réalisée sous agitation continue pendant 24h, et la quantification a été effectuée par spectroscopie UV-Visible, en mesurant l'absorbance correspondant aux chromophores caractéristiques respectivement de la carbamazépine et du tramadol.

Chapitre 3 : Produits pharmaceutiques dans les zones de rétention : Effets de la composition et de l'accumulation de la phase particulaire

Le Chapitre 3 présente les résultats d'une étude menée à l'échelle de l'étang de la Beulie, et s'intéresse aux effets de la composition et de l'accumulation de la phase particulaire dans l'étang sur la distribution spatiale des PPs adsorbés sur les sédiments d'interface. En effet, les chapitres précédents ont permis de faire l'inventaire des matrices présentes dans les masses d'eau. On y retrouve des éléments sous forme dissoute, mais également sous forme particulaire. Certaines de ces matrices sont connues pour être particulièrement réactives, à l'instar de la matière organique et de certains minéraux comme les argiles. En contexte péri-urbain, les cours d'eau sont bien souvent alimentés en partie par les effluents des stations d'épuration, entraînant ainsi l'émission de traceurs d'origine anthropique, tels que les produits pharmaceutiques (PPs), dans le milieu naturel. Les PPs sont des molécules pouvant avoir un caractère hydrophile comme hydrophobe, et dont les caractéristiques physico-chimiques sont déjà très bien documentées dans la littérature. De plus en plus d'études se sont intéressées à leur quantification sur la phase particulaire, cette affinité étant susceptible d'avoir une influence importante sur leur devenir dans le milieu naturel. Si la plupart des études ont principalement ciblé les matières en suspension dans les cours d'eau comme phase porteuse des PPs, ces dernières années ont vu croître progressivement le nombre de travaux caractérisant les PPs dans la phase particulaire accumulée dans les zones de rétention. En effet, les zones de rétention constituent un réceptacle pour les matières en suspension, qui sédimentent par rupture du courant, y compris pour les PPs qu'elles sont susceptibles de porter. L'échantillonnage de la phase particulaire dans les zones de rétention se limite bien souvent au prélèvement de carottes sédimentaires, voire une seule carotte sédimentaire, représentant une archive temporelle du dépôt des PPs. Cependant, ce type de méthode ne permet pas d'attester de la représentativité spatiale des échantillons, risquant même de diluer

l'information en passant à côté d'une zone de fortes teneurs en PPs, autrement dit un « hotspot ». Outre la distribution spatiale des teneurs en PPs, celle des différentes matrices composant la phase particulaire accumulée peut également être variable, suivant les mécanismes de dépôt et de diagenèse du sédiment.

Ce chapitre propose ainsi de questionner la distribution spatiale des matrices du sédiment et des PPs à l'interface eau-sédiment, en réalisant un échantillonnage à haute résolution spatiale à l'échelle de la zone de rétention complété par des caractérisations granulométriques, géochimiques et minéralogiques fines des différentes matrices du sédiment et des PPs. Il interrogera également les facteurs pouvant influencer cette distribution spatiale, qu'ils soient d'ordre morphologique ou physico-chimique.

Cette étude a été réalisée à l'échelle de l'étang de la Beulie, situé sur le bassin versant de l'Egoutier, en aval de la station d'épuration d'un hôpital psychiatrique, dont les effluents sont une source confirmée de PPs dans l'Egoutier. L'échantillonnage de l'étang a permis de collecter 43 échantillons de sédiments d'interface entre 2018 et 2023.

Les résultats acquis dans le cadre de cette étude ont fait l'objet d'une publication dans *Applied Geochemistry* en 2025, présentée ci-après.

Les résultats de cette étude mis en évidence une distribution spatiale hétérogène des teneurs en PPs et des matrices du sédiment d'interface à l'échelle de l'étang de la Beulie. Ils ont plus particulièrement permis d'identifier le delta de l'étang (zone amont) comme hotspot de PPs, notamment neutres, et de carbone organique total (COT). De plus, les résultats de l'approche statistique ont montré que les teneurs des PPs neutres et des PPs cationiques ne covariaient pas à l'échelle de l'étang, suggérant des modes d'adsorption différents et/ou des phases porteuses différentes. L'étude a également permis de souligner des différences de typologie et d'état de dégradation de la matière organique entre le delta et le bassin principal de l'étang, et des distributions granulométriques de sédiment également différentes entre ces deux zones. Ceci suggère un mécanisme double, avec d'une part les processus classiques de sédimentation dépendant à la fois de la taille et de la densité des particules et de la différence de températures entre l'eau du ru et celle de l'étang, et d'autre part la diagenèse du sédiment, en grande partie dépendante des conditions physico-chimiques dans la colonne d'eau et notamment à l'interface eau-sédiment, elles aussi hétérogènes entre le delta et le bassin principal.

Si cette étude a permis d'identifier une zone d'accumulation préférentielle des PP à l'échelle de l'étang, et d'en dégager les caractéristiques granulométriques, géochimiques et minéralogiques principales, elle soulève à présent la question de la répartition des PP au sein du sédiment situé dans cette zone. Ce dernier est caractérisé par une distribution granulométrique hétérogène avec une contribution non négligeable de la fraction grossière >1 mm, des concentrations moyennes en COT plus importantes qu'ailleurs dans l'étang et par une typologie mixte de la MO, d'origine principalement terrigène dans cette zone. Ces caractérisations ont cependant été réalisées sur du bulk, signifiant le sédiment dans son entièreté. La distribution granulométrique hétérogène du sédiment, à l'origine de modes de sédimentation différents, invite ainsi à étudier la composition des différentes classes granulométriques, et la distribution des PP dans ces classes, en comparaison avec celle de la matière organique. Ceci permettrait en effet de déterminer les caractéristiques plus précises de la matière organique, matrice réactive du sédiment susceptible de jouer un rôle important dans le devenir des PP, dans différentes classes granulométriques, pouvant être témoins d'une origine différente ou d'un état de décomposition différent. L'objectif serait plus particulièrement d'appréhender l'origine de l'affinité entre la MO et les PP, et sa stabilité au regard des conditions physico-chimiques de la colonne d'eau.

Chapitre 4 : Produits pharmaceutiques dans les sédiments d'interface : lien avec la typologie et les propriétés réactives de la matière organique

Le Chapitre 4 propose d'étudier l'adsorption des PP sur les sédiments d'interface au regard de la composition, de la typologie et des propriétés réactives de la MO, faisant suite au Chapitre 3 ayant mis en évidence le rôle potentiel de la MO dans la concentration des PP sur la matrice sédimentaire. En effet, soumise à la diagénèse précoce, la MO sédimentaire est susceptible de voir sa composition et sa réactivité évoluer, ainsi que sa capacité à porter des PP.

Etant donné que les sédiments du delta de l'étang sont concentrés en COT et en PP (cf Chapitre 3), cette zone a été particulièrement caractérisée. Un profil de physico-chimie, comprenant les mesures du pH, de l'Eh, de la conductivité électrique et de l'O₂ dissous, a été réalisé depuis la surface jusqu'à l'interface eau/sédiment avec une mesure tous les 5 cm de profondeur, et les sédiments et l'eau ont été collectés à l'interface eau/sédiment.

Les sédiments ont été tamisés afin de les séparer en 5 fractions granulométriques (>1 mm ; 250 µm-1 mm ; 160 µm-250 µm ; 63 µm-160 µm ; <63 µm). La MO de chaque fraction a été quantifiée par mesure du COT par pyrolyse Rock-Eval. La déconvolution des courbes S2 obtenues par pyrolyse Rock-Eval ont permis de décompter 4 fractions de MO. Les mesures par spectroscopie infrarouge à transformée de Fourier (FTIR) ont permis d'identifier les groupes fonctionnels principaux de la MO.

Les résultats ont montré une concentration en COT et en PPs plus importante dans la fraction >1 mm que dans la fraction <63 µm. Pourtant, la fraction <63 µm est généralement préférentiellement étudiée du fait de sa surface spécifique plus élevée. L'indice hydrogène a également affiché une valeur plus importante dans la fraction >1 mm que dans la fraction <63 µm, suggérant une meilleure préservation de la MO dans la fraction >1 mm. La comparaison de la composition en groupes fonctionnels de la MO dans ces deux fractions a permis de mettre en évidence la présence de polysaccharides, notamment associés à la cellulose et autres matériaux dérivés de la végétation, dans la fraction >1 mm, et pas dans la fraction <63 µm, ce qui est cohérent avec la composition générale de la fraction >1 mm comprenant des débris végétaux. Or, la cellulose est connue pour son affinité pour les molécules pharmaceutiques, et pour la stabilité de cette affinité sur une large gamme de valeur de pH (Liu et al., 2021). La cellulose est par ailleurs notamment utilisée en pharmacologie comme liant. La déconvolution des courbes S2 a mis en lumière une proportion plus élevée de la fraction F3 dans la fraction >1 mm que dans la fraction <63 µm, et inversement pour la fraction F4, ces deux fractions organiques étant usuellement associées aux substances humiques et aux géo-macromolécules matures, respectivement, dont la présence a également été soutenue par l'identification des groupes fonctionnels suite aux mesures FTIR. L'ensemble de ces résultats suggère une meilleure prédisposition de la MO contenue dans la fraction >1 mm que celle contenue dans la fraction <63 µm à créer des liaisons avec les PPs, expliquant leur concentration plus importante dans la fraction >1 mm.

Les PPs ont également été quantifiés dans les eaux de tamisage récupérées par centrifugation de la fraction <63 µm, après les tamisages humides utilisant soit de l'eau ultra-pure, soit de l'eau prélevée à l'interface eau/sédiment. Le calcul des masses totales en PPs dans les volumes d'eaux utilisées et récupérées a montré des quantités plus importantes en tramadol (TRA) et en venlafaxine (VFX) dans les eaux utilisées que dans les eaux récupérées, et inversement pour la carbamazépine, (CBZ) et l'oxazépam (OXA) et le diazépam (DIA). La fluoxétine (FLX) n'a pas été détectée en phase dissoute. Ces résultats suggèrent une

adsorption du TRA et de la VFX et une désorption de la CBZ, de l'OXA et du DIA de la phase particulaire pendant les tamisages humides. Ce processus était par ailleurs intensifié lors de l'utilisation de l'eau ultra-pure. Une hypothèse pouvant expliquer ce changement de phase porteuse peut être le changement de conditions physico-chimiques. Le pH de l'eau ultra-pure se situe généralement entre 1 et 2 unités en-dessous de 7, et celui de l'eau de l'étang était à 7,5. Les pKa du TRA, de la FLX, de la VFX, de la CBZ, de l'OXA et du DIA étant respectivement 9,4, 9,8, 8,9, 2,3, 11,6 et 3,9, le changement de pH est peu susceptible d'avoir modifié la charge des molécules. En revanche, les deux eaux utilisées pour le tamisage étaient très oxygénées par rapport à celle de l'interface eau/sédiment, dont le pourcentage d'O₂ dissous était proche de zéro. La mesure de l'Eh à l'interface confirme par ailleurs des conditions anoxiques. Or, l'étude menée sur la stabilité thermodynamique de la MO a montré que, dans les conditions Eh à l'interface (Eh = -39 mV), l'activité relative de la MO contenue dans la fraction >1 mm était plus importante que celle de la MO contenue dans la fraction <63 µm, suggérant une meilleure stabilité de la MO contenue dans la fraction >1 mm en condition anoxique. Dans les conditions d'oxygénation du tamisage à l'eau ultra-pure, qui représentent une gamme de Eh entre 200 et 400 mV, il est plus difficile d'attribuer la plus haute activité relative, puisque celles des MO contenues dans les deux fractions présentent chacune une tendance maximale et une tendance minimale sur cette gamme d'Eh. Cependant, les concentrations en PPs plus importantes sur la fraction >1 mm suggèrent une meilleure résistance des liaisons entre cette fraction et les PPs lors du tamisage. Les comportements des PPs lors du tamisage soulève la question de la réversibilité du piégeage des PPs sur les sédiments d'interface. En effet, un changement de condition d'oxygénation a également été observée dans le milieu naturel, à l'interface eau/sédiment en septembre 2023, ce qui rend envisageable des processus d'adsorption/désorption dans le milieu naturel, tels que ceux observés lors des tamisages humides.

Le Chapitre 4 a ainsi mis en évidence l'importance du rôle joué par la composition, la typologie et les propriétés réactives de la MO sur le comportement des PPs dans le continuum eau-sédiment. Il a également confirmé la pertinence de la caractérisation de la MO et des PPs dans différentes fractions granulométriques du sédiment, auxquelles il est possible d'attribuer le rôle de sentinelles de l'état de dégradation de la MO sédimentaire, jouant sur sa capacité à créer des liaisons avec les PPs.

Chapitre 5 : Stabilité du piégeage des produits pharmaceutiques sur les sédiments d'interface : facteurs influençant les mécanismes d'adsorption et leur potentielle réversibilité

Dans la continuité du Chapitre 4, le Chapitre 5 a exploré tout d'abord les facteurs pouvant jouer sur la réversibilité des processus d'adsorption entre les PPs et le sédiment d'interface. Pour ce faire, des expériences d'interaction avec agitation continue entre du sédiment et de l'eau d'interface ont été réalisées pour suivre cinétiquement les dynamiques d'échanges des PPs entre les phases dissoute et particulaire, par des prélèvements de la phase dissoute à intervalles de temps réguliers (0 min, 10 min, 30 min et 60 min). Ensuite, afin d'explorer la potentielle synergie pouvant opérer entre les matrices du sédiment d'interface, en particulier la MO et la kaolinite, une série d'expériences en batchs a été mise en œuvre avec pour phases solides du sédiment de la Beulie, ou de la kaolinite ou un mélange des deux phases, et pour phase dissoute une solution de molécules pharmaceutiques, la CBZ ou le TRA, à des concentrations supérieures à celles du milieu naturel.

Les résultats obtenus pour l'expérience cinétique ont montré une diminution rapide (10 min) des concentrations du TRA et du PAR dans la phase dissoute, une augmentation rapide de la concentration de la CBZ, une augmentation par paliers pour l'OXA et le DIA, et enfin une diminution suivie d'une augmentation pour le DIC. Concernant le TRA, la CBZ et l'OXA, les résultats révèlent une adsorption du TRA et une désorption de la CBZ et de l'OXA, ce qui confirme les discussions du Chapitre 4. Concernant le PAR, qui est une molécule neutre sur la gamme de pH étudiée, les résultats sont en opposition avec ceux obtenus à l'issu des tamisages humides (Appendix 6). Les cinétiques en deux étapes, telles que celles observées pour l'OXA, le DIA et le DIC ont déjà été observées. Ce type de cinétiques peut également s'expliquer par une compétition entre les PPs et les autres espèces ioniques pour les sites d'adsorption (Grabic et al., 2022), comme montré par l'évolution de la conductivité électrique, qui témoigne d'augmentations et de diminutions de la concentration en espèces ioniques au cours de l'heure de l'expérience. Cela soutient l'hypothèse d'une hiérarchie entre les PPs, régie par leurs propriétés physico-chimiques et par la force des liaisons qu'ils créent avec la phase particulaire, et d'autre part par la composition de la phase dissoute. Cela implique un grand nombre de facteurs, souvent difficile à suivre ou à reproduire expérimentalement. C'est pourquoi certaines études encouragent l'utilisation complémentaire d'approches numériques à l'image des simulations moléculaires (Schaumann and Thiele-Bruhn, 2011). Cependant, ces

simulations moléculaires nécessitent au préalable une caractérisation fine des phases porteuses, en particulier la MO (Ahmed et al., 2012).

Les résultats de l'expérience en batch ont permis de montrer, aussi bien dans le cas du TRA que de la CBZ, une meilleure adsorption plus importante sur le sédiment d'interface que sur la kaolinite seule. Comme la kaolinite est une des phases contenues dans le sédiment d'interface, ce résultat confirme l'action d'une autre phase porteuse que la kaolinite pour l'adsorption de la CBZ et du TRA. Dans le cas de la CBZ en particulier, il a également été observé que la concentration moyenne adsorbée lorsque la phase solide était composée d'un mélange de sédiment et de kaolinite était similaire à celle adsorbée dans le cas du sédiment seul. Bien que l'erreur de reproductibilité ne soit pas négligeable, ce résultat, qui va dans le sens d'une synergie entre le sédiment et la kaolinite à l'image de la formation de complexes organo- minéraux, encourage à explorer plus en profondeur le potentiel de formation de ces complexes. De plus, une étude en batch également menée sur la CBZ a montré la plus forte adsorption de la CBZ par des complexes acides humiques - kaolin que celle par les deux phases lorsqu'elles étaient présentes seules (Wang et al., 2018). Dans le cas du sédiment d'interface, si ce processus est avéré, il se peut qu'il soit atténué par la présence d'autres phases non réactives avec les PPs telles que le quartz (*cf* Chapitre 3).

Afin d'étudier plus en détail les interactions entre MO et kaolinite, une autre approche expérimentale sous forme de batch avec de la léonardite, qui est un acide humique de référence et de la kaolinite est présentée en Annexe 7. Les résultats, non exploitables en l'état, n'ont pas été présentés dans ce Chapitre, l'expérience nécessitant des améliorations expérimentales et de quantification des PPs en phase dissoute.

Ce chapitre 5 a révélé des cinétiques d'adsorption/désorption différentes entre les PPs, attribuées d'une part aux propriétés physico-chimiques des PPs et d'autre part à la complexité de la matrice sédimentaire et de la matrice aqueuse. Ceci a été confirmé par des expériences en batch, qui ont montré d'une part la meilleure adsorption des PPs sur du sédiment comparativement à une phase « pure » de kaolinite, et d'autre part la potentielle synergie existante entre les différentes matrices du sédiment, en particulier la MO et la kaolinite. Ce chapitre permet ainsi une prise de recul sur l'élaboration d'expériences telles que celles en batch, qui isolent bien souvent les différentes phases porteuses d'intérêt. Si cette approche est nécessaire dans un premier temps pour déterminer les propriétés intrinsèques des différentes matrices, elle est rarement suffisante à l'intégration des processus biogéochimiques influençant les échanges au sein du continuum eau-sédiment. L'utilisation

de méthodes numériques peut permettre d'acquérir des données complémentaires à celles obtenues expérimentalement, mais la paramétrisation reste bien souvent également limitée compte-tenu de la complexité du milieu naturel.

Conclusions générales, limites et perspectives

L'ensemble des résultats acquis dans le cadre de cette thèse ont montré que :

- L'étang de la Beulie agit comme une zone d'accumulation sédimentaire et de PPs adsorbés sur la phase particulaire. Une distribution spatiale hétérogène a été mise en évidence pour les concentrations en matrices du sédiment d'interface susceptibles d'avoir une affinité pour les PPs, telles que la MO et la kaolinite, ainsi que pour les concentrations en PPs. Cette distribution spatiale a par ailleurs permis d'observer une covariance spatiale entre les concentrations en PPs et celles en COT, suggérant une affinité des PPs pour la MO.
- La détermination des conditions physico-chimiques à l'interface eau/sédiments dans le delta de l'étang ont montré des conditions d'oxygénation différentes entre 2023 et 2024.
- La MO sédimentaire présente une typologie, une composition et des propriétés réactives différentes selon la granulométrie du sédiment d'interface. La fraction >1 mm présentait par ailleurs des concentrations en PPs plus importantes que la fraction <63 μm , possiblement en lien avec les propriétés différentes de la MO entre ces fractions.
- La méthode de tamisage humide réalisée afin de séparer le sédiment en différentes fractions granulométriques a mis en évidence une désorption de PPs neutres et une adsorption de PPs cationiques, possiblement en lien avec l'oxygénation de l'eau utilisée. Ceci questionne la réversibilité du piégeage des PPs sur la matrice sédimentaire dans le milieu naturel, où des conditions d'oxygénation différentes ont été observées entre 2023 et 2024 à l'interface eau/sédiment.
- Les cinétiques d'adsorption/désorption des PPs sur la matrice sédimentaire étaient différentes selon les PPs, présentant dans certains cas des paliers, possiblement en lien avec la composition chimique de l'eau d'interface, et avec la compétition pouvant avoir lieu entre les PPs et les autres espèces ioniques en solution.
- L'adsorption des deux PPs utilisés pour les batchs, la CBZ et le TRA, sur une matrice complexe (sédiment d'interface) était supérieure comparée à celle sur une matrice « pure » (kaolinite), montrant l'implication d'autres composants du sédiment dans l'adsorption des PPs, tels que la MO. Dans le cas de la CBZ, la formation de complexes organo- minéraux pourraient notamment expliquer la meilleure adsorption sur les matrices complexes.

La démarche scientifique a montré que :

- Un échantillonnage à haute résolution spatiale est nécessaire à la prise en compte de l'hétérogénéité spatiale de la matrice sédimentaire.
- La caractérisation exhaustive de la MO en particulier a permis d'en déterminer les fractions les plus réactives dans les différents compartiments granulométriques de la matrice sédimentaire.
- Une approche expérimentale en batch avec des matrices naturelles et pures a mis en évidence la synergie œuvrant au sein des matrices complexes naturelles par rapport aux matrices pures.
- L'approche couplée terrain-laboratoire est nécessaire à la bonne compréhension du devenir des PP dans l'environnement, car elle permet la détermination des différents mécanismes en jeu en prenant en compte la complexité du milieu naturel.

Les différentes limites de cette étude et de la démarche scientifique sont :

- La détermination incomplète et biaisée de la distribution des PP dans les différentes fractions granulométriques du sédiment due au tamisage humide empêche d'effectuer un bilan de masse précis.
- La complexité des matrices dissoutes et particulières naturelles, l'eau et le sédiment d'interface, ne permet pas de comprendre expérimentalement tous les mécanismes en jeu dans l'adsorption des PP sur la phase particulaire, ni leur désorption. D'autres facteurs, tels que la composition ionique de l'eau d'interface ou la formation de complexes entre plusieurs phases porteuses, tels que la MO et les minéraux argileux, peuvent en effet influencer les cinétiques et les mécanismes d'adsorption.
- La fraction colloïdale (3,5 kDa-0,45 μm) n'a pas été étudiée à part entière dans cette thèse, malgré son rôle connu dans la remobilisation des contaminants. L'expérience en sac à dialyse présentée en Annexe 7 a également montré la difficulté de la détermination de la formation de complexes entre des colloïdes (ici de léonardite, acide humique) et les PP, ces complexes étant peu stables.
- Dans le milieu naturel, les PP sont également quantifiés sur la fraction particulaire en aval de l'étang de la Beulie, ce qui montre le piégeage incomplet dans l'étang. De plus, les variations de conditions d'oxygénation à l'interface eau/sédiment au cours de l'année rendent difficile l'élaboration d'un bilan de masse précis sur le devenir des PP dans le continuum eau-sédiment.

Ce travail de thèse a ouvert la voie à diverses perspectives :

- Le rôle joué par la matière organique, ainsi que par la formation de complexes organo-minéraux, dans l'adsorption des PPs sur la phase particulaire pourrait être étudié plus en détail en extrayant les molécules organiques d'intérêt, et en les complexant avec des phases minérales (argiles, oxydes), en réalisant ensuite des isothermes d'adsorption avec différents PPs afin d'évaluer la capacité d'adsorption de ces phases, de même que la compétitivité pouvant exister entre les PPs suivant leurs caractéristiques (charges, groupes fonctionnels).
- L'étang de la Beulie s'est avéré être une zone de rétention de la phase particulaire, mais également un hotspot de PPs, bien qu'étant un piège imparfait. Les PPs sont effectivement quantifiés dans les matières en suspension en aval de l'étang, et les Chapitres 4 et 5 ont par ailleurs permis de souligner le caractère réversible de leur adsorption sur la phase particulaire. Un développement pouvant être imaginé afin d'endiguer la diffusion des PPs dans le milieu naturel serait de mettre en place des zones de rétention en conditions contrôlées (flux entrant et sortant de matières organiques, contrôle des conditions physico-chimiques).

General Introduction

Together, the lithosphere, the pedosphere, the hydrosphere, the biosphere and the atmosphere constitute a continuum that hosts mass and energy transfers. These transfers are responsible for the hydrological and biogeochemical cycles that occur in the near-surface environment. This continuum is named the « Earth Critical Zone » (ECZ, US National Research Council, 2001; Anderson et al., 2004). The ECZ has been particularly studied these last decades, in a context where an increasing number of factors are likely to impact erosion rates, the ecological state of waterbodies, biodiversity and air quality, to name a few. These factors, including climate change, pollution, soil occupation and land use are part of a relatively recent era: the Anthropocene, corresponding to the period in which the human footprint began to have a significant global environment impact (Crutzen and Stoermer, 2000; Ruddiman, 2013). The long-term preservation of the environment is directly linked with socio-economic sustainability, as evidenced by issues such as water and food supplies, and environmental hazards like wildfires and extreme flood events (Banwart et al., 2013). Therefore, it is challenging to determine how the ECZ responds to these different anthropogenic pressures, and evaluate its resilience. This resulted in the establishment of research infrastructures such as the French OZCAR network (Critical Zone Observatories: Research and Application), which brings together French observation sites focused on surveying the ECZ (Gaillardet et al., 2018).

The biogeochemical cycles are controlled by the chemical, biological and physical processes occurring between the various compartments of the ECZ (Gaillardet et al., 2018), particularly soils and streams. Apart from their roles in humification processes, carbon storage and hosting biota (Wild, 1993), soils also supply surface water (Moldan and Cerny, 1994). Indeed, they participate in the discharge of groundwater into streams, and constitute the source of weathering and erosion products, which end up as suspended particulate matter (SPM) in surface water (Nelson, 1973). SPM notably constitutes an important source of organic carbon in streams (Manninen et al., 2023) and contributes to the carbon cycle (Luo et al., 2022). Considering the particulate phase in biogeochemical cycles is a relatively recent development, despite its significant contribution to mass-balances (Turner and Millward, 2002; Oelkers et al., 2011). The transfer of particles in streams depends on the size, the morphology and the connectivity of watersheds, as well as the intensity of hydrological events such as rainfall, which drive the solid charge of streams (Römkens et al., 2002). Particles can be transported to

the outlet of catchments, but they can also settle in retention areas, such as lakes and ponds. This creates a rupture in the sedimentary cascade (Ledieu et al., 2020). Furthermore, the sequestration of sediments and their diagenesis in retention areas can lead to the remobilisation of elements in the aqueous phase, thereby modifying their distribution between aqueous and particulate phases (Hou et al., 2025). These potential changes in the carrying phases and speciation of elements made surveying biogeochemical cycles in the aqueous-particulate continuum essential.

To survey these transfers of water and particles, watersheds have been progressively instrumented, and national observation services have been set up (Gaillardet et al., 2018; Pierret et al., 2018; Gogo et al., 2021). Watersheds are studied from various angles, including hydrogeology, pedology, geochemistry and biology. The aim is to determine and quantify the factors influencing particulate and aqueous fluxes, in order to calculate the mass balance necessary to trace and reconstitute the evolution of the biogeochemical cycles at the watershed scale and over decades (Moldan and Cerny, 1994).

In addition to soil artificialisation, which increases their vulnerability to extreme hydrological events, the increasing urbanisation of watersheds - referred to as “suburban” watersheds - has introduced another form of anthropogenic pressure: the emission of tracers from anthropogenic origin (named anthropogenic tracers: AT, Pascual-Aguilar et al., 2015). AT include heavy metals (Murray et al., 2004), microplastics (Dris et al., 2015), polycyclic aromatic hydrocarbons (Song et al., 2015), and pesticides, as well as per-and-polyfluoroalkyls substances (PFAS, Xu et al., 2024). These AT enter the environment through various ways, including industrial processes (Qin et al., 2022), land-use (Pérez et al., 2021), wastewater treatment plants emissions (Santos et al., 2013; Jacob et al., 2020) and road infrastructures (Hanna et al., 2009; Liu et al., 2014). The increase in the solid charge in streams, coupled with the emission of AT, whose affinity for the particulate phase has been verified in many studies (Demirak et al., 2006; Bai et al., 2021; Le Gaudu et al., 2022), support investigating AT under both aqueous and particulate forms. Indeed, their environmental pathways and fate depend on their persistence and bioavailability, and therefore on the distance they can be transferred. The last few decades have also been marked by a growing concern about persistent organic pollutants (POPs). Moreover, the Stockholm Convention emphasised on the need to study the behaviour of other POPs, such as PPs, in the environment (Mbengue, 2001).

Significant progress was made in medication in the second half of the 20th century. A growing number of pharmaceutical products (PPs) were developed, reaching more than 3,000

now in existence (Medication and Environment Report, French Pharmacology Academy, 2019). The products were designed to be effective even at very low concentrations (Hernando et al., 2006). Once excreted by the human body, some of these molecules have been found to remain active, even after wastewater treatment procedures (Aminot et al., 2015; Paiga et al., 2016). The increasing number of studies investigating their occurrence or fate in recent decades is justified by their potential toxicity and persistence in the natural environment (da Silva et al., 2011; Afonso-Olivares et al., 2017; Castano-Ortiz et al., 2024). While most PPs are hydrophilic, many of them have been quantified in soils, sediments and SPM at concentration of great concern (Thiebault et al., 2021; Ledieu et al., 2021). Although no official concentration thresholds exist for PPs (in comparison with those existing for heavy metals for example), their impact on living organisms, like the resistance of bacterial communities to antibiotics (French Pharmacology Academy, Avis Prop. loi Pénuries, 2024) have been verified even at low particulate and dissolved concentrations (a few ng/g and ng/L, respectively). As their interaction with the particulate phase can limit or enhance their transfer in the natural environment (Löffler et al., 2005), establishing their distribution within the aqueous-particulate continuum has become a key scientific issue.

Studies investigating the fate of ATs such as PPs in the environment often focus on “large-scale” (more than 100 km²) catchments that incorporate extensive urban areas (da Silva et al., 2011; Perez et al., 2022). However, recent studies (Boulard et al., 2020; Ledieu et al., 2021; Thiebault et al., 2017) have found that “small-scale” watersheds (< 5-10 km²) exhibit relatively high potential in terms of anthropogenic pressure. Indeed, they are more vulnerable to extreme events due to their faster response (Wang et al., 2019). Furthermore, as their streams are partially fed by the effluents of wastewater treatment plants, the dilution of ATs once emitted into the stream can vary, depending on the hydrological regime. As concentrations of effluents in PPs can reach several µg/L (Santos et al., 2013; Ledieu et al., 2021), a lower dilution by stream water could have an even more severe impact on the natural environment.

There is still a lack of data explaining the precise interactions between PPs and the aqueous-particulate continuum. Although a growing number of studies have investigated the fate of PPs adsorbed onto sediments and SPM, only a few have deciphered the reactive sediment matrices that are likely to carry PPs. Furthermore, few studies have examined the fate of PPs in relation to sediment diagenesis, particularly in retention areas where sediments accumulate. This questions about the stability and reversibility of PPs adsorption onto the

particulate phase, which directly affects their mobility and persistence over time in the natural environment.

Objectives of the present work

The present work is part of the TRANSAT APR IA research project “Transfert particulaire des contaminants en bassin versant anthropisés” (Contaminant particulate transfers in anthropised watersheds), founded by the Region Centre-Val-de-Loire and led by Anaëlle Simonneau. The project aimed to investigate the behaviour of emerging contaminants, namely pharmaceutical products (PPs), in the water-sediment continuum at the catchment scale. The Egoutier watershed (Semoy, Loiret, France), hosting the OBSCURE instrumented site and part of the SNO Observil has been surveyed in this purpose. The present work focuses on the Beulie pond, a suburban retention area belonging to the Egoutier watershed, located downstream of wastewater treatment plant effluents, and where physico-chemical processes occurring (i.e. pH and redox trends) can affect both the sorption and the speciation of PPs. My PhD research aims to identify and discuss the interactions between PPs and the reactive phases of the water-sediment continuum, that are likely to adsorb or form complexes with them.

The main objectives are:

- 1) To determine the processes driving the spatial distribution of the matrices that compose surface sediments and of PPs at the Beulie pond scale
- 2) To identify the potential carrier phases of PPs within the water-sediment continuum, and to determine the factors responsible for this affinity
- 3) To decipher the adsorption/desorption mechanisms between PPs and their carrying phases
- 4) To explore the role of physico-chemical parameters, particularly pH, redox potential, electrical conductivity and dissolved oxygen, in sediment organic matter diagenesis and as a consequence in the stability/reversibility of PPs trapping within pond surface sediments.

The scientific approach relies on a field and lab combination, including a high-resolution sampling of the water/sediment interface of the Beulie pond, located in the Egoutier watershed, the seasonal physico-chemical characterisation of the water-column from the surface to the water/sediment interface, the analytical characterisation of particulate and aqueous matrices at the pond scale, and the elaboration of batch sorption experiments between surface sediment matrices and pure PPs solution.

Organisation of the manuscript

The present manuscript is organised into five chapters.

Chapter 1 describes the sources, composition and geochemical reactivity of the main matrices present in waterbodies, and likely to interact with PPs, in suburban context. It also presents the chronology of studies performed on the occurrence and fate of PPs in the natural environment, and explains why it is important to perform these studies also in small-scale watersheds.

Chapter 2 presents the field sampling, analytical and experimental strategies and also explains the relevance of the Beulie pond as being the investigated area.

Chapter 3 explores the spatial distribution at the Beulie pond scale of contents in surface sediments matrices, such as organic matter and clays, and in PPs and discusses the effect of sediment composition and accumulation on the spatial distribution of PPs. This work has been published as a research paper in *Applied Geochemistry* in 2025: *Humbrecht, A., Simonneau, A., Thiebault, T., Bernier-Turpin, G., Le Milbeau, C., Veselská, V., ... & Le Forestier, L. (2025). Effect of sediment composition and accumulation on pharmaceutical product spatial distributions at the suburban pond scale (Beulie pond, SNO Observil, France). Applied Geochemistry, 190(10648), 7.*

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Chapter 4 investigates the properties of OM in surface sediments, such as its composition in functional groups and reactivity, which are likely to explain its apparent affinity for PPs. This work has been written as a research paper to be submitted to *Environmental Research*.

Chapter 5 explores the stability of PPs trapping within surface sediments, and the factors which are likely to drive adsorption and desorption processes. It therefore proposes a preliminary experimental approach, studying adsorption/desorption mechanisms and kinetics.

Chapter 1. Suburban water bodies: origin, forms and fate of their natural reactive matrices and their anthropogenic tracers in the literature



Water bodies are part of the anatomy of the catchment. We distinguish between moving water bodies, like streams, from stagnant ones, like lakes, ponds and retention areas in general. These water bodies are participating to the topography of the catchment and are thus playing a role in water residence time (McGuire et al., 2005). Water courses can be fed by both rainwater and groundwater, while retention areas collect streams, with possible input of groundwater and or rainwater. Water bodies can be divided into compartments (Figure 1.1). Indeed, water bodies result from the passing or stagnation of water, most of the time over a layer of sediments, either named “bedload sediments” when referring to streams or “surface sediments” when referring to the water/sediment interface of retention areas. Those sediments are originating from the erosion of soils, suggesting that before settling in the bedload of the stream or in the retention area, they have been transported as suspended particulate matters (SPMs). The occurrence of SPMs in water bodies is the result of soils erosion by streams (Nelson, 1973). Their characteristics, including their abundance, form, composition and reactivity are spatially and temporally variable as they are directly related to both soil composition and catchment hydrodynamics (Moldan and Cerny, 1994).

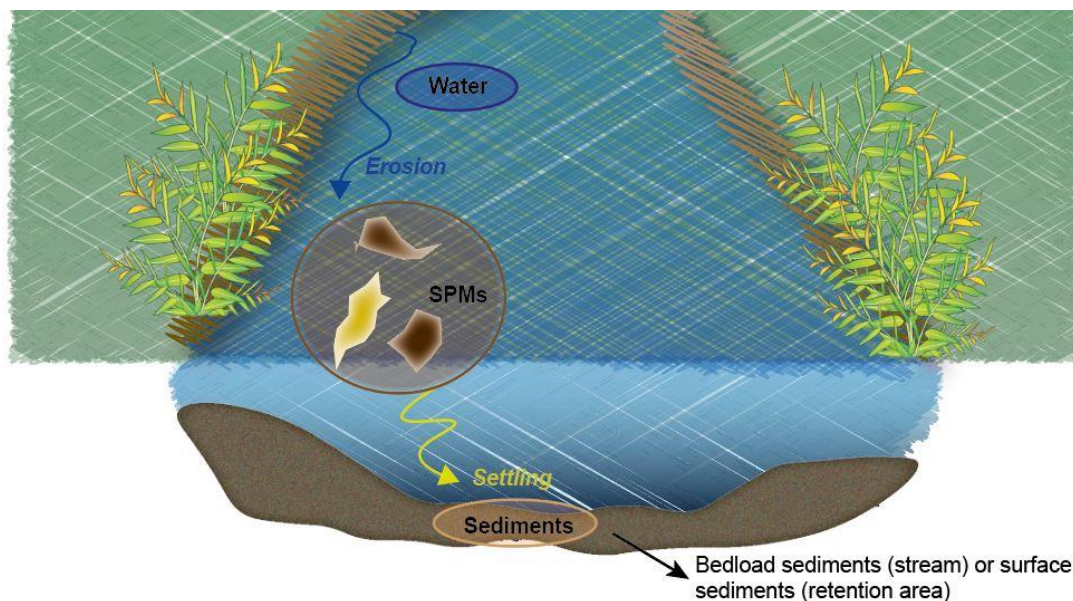


Figure 1. 1: Compartments considered in water bodies: water, suspended particulate matters (SPMs) and (bedload or surface) sediments. Not to scale.

The specificity of suburban streams is that they can be fed by “grey water” of anthropogenic origin, often corresponding to the discharges of wastewater treatment plants (WWTPs) (Figure 1.2). This involves the emission of elements and compounds of anthropogenic origin into the natural environment, including trace elements, organic compounds such as pesticides, polycyclic aromatic hydrocarbons, pharmaceutical products,

and potentially many others depending on the origin of the effluents (*cf* General Introduction). Once introduced into the water body, these elements and compounds may be transported and/or interact with SPMs. Their affinity for SPMs and the transfer of SPMs through catchments thus determine their fate in the environment.

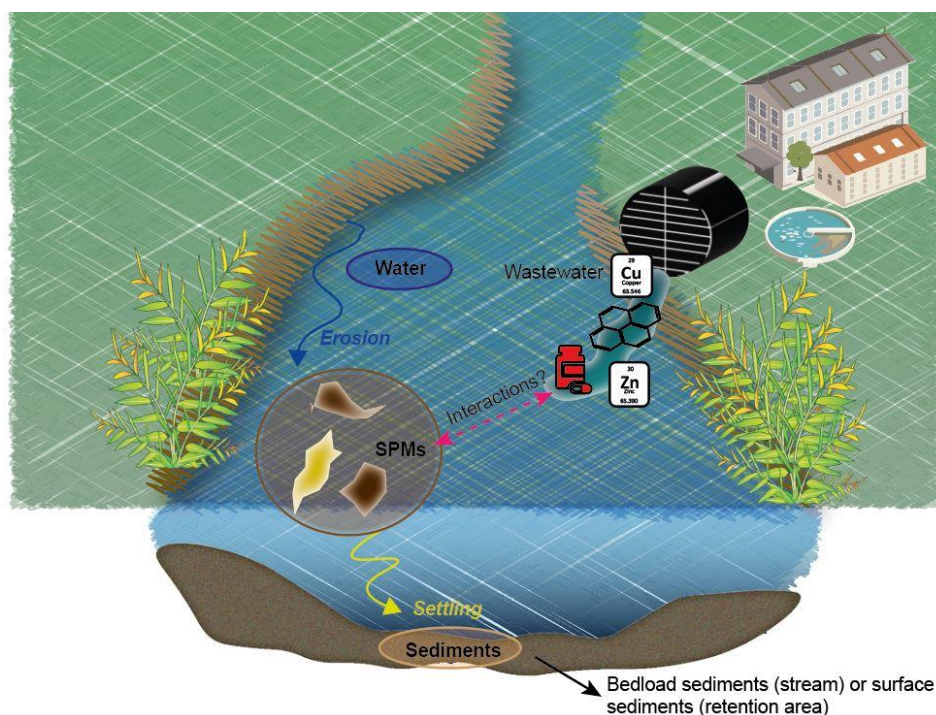


Figure 1. 2: Anthropogenic effluent discharge in suburban water bodies. Not to scale.

An increasing interest in the particulate matrix has been noticed in recent decades. Indeed, many studies have demonstrated the potential of SPMs to carry anthropogenic tracers (Hart, 1992; Nie et al., 2015; Boulard et al., 2020; Niu et al., 2021; Liu et al., 2024). The Water Framework Directive (DCE, 2000) has even identified SPMs as “pollutants”, although they are actually vectoring pollutants (Figure 1.2). The potential affinity of water and SPMs for anthropogenic tracers depends mainly on the reactive matrices that are part of their composition and on the fate of these matrices (Figure 1.3).

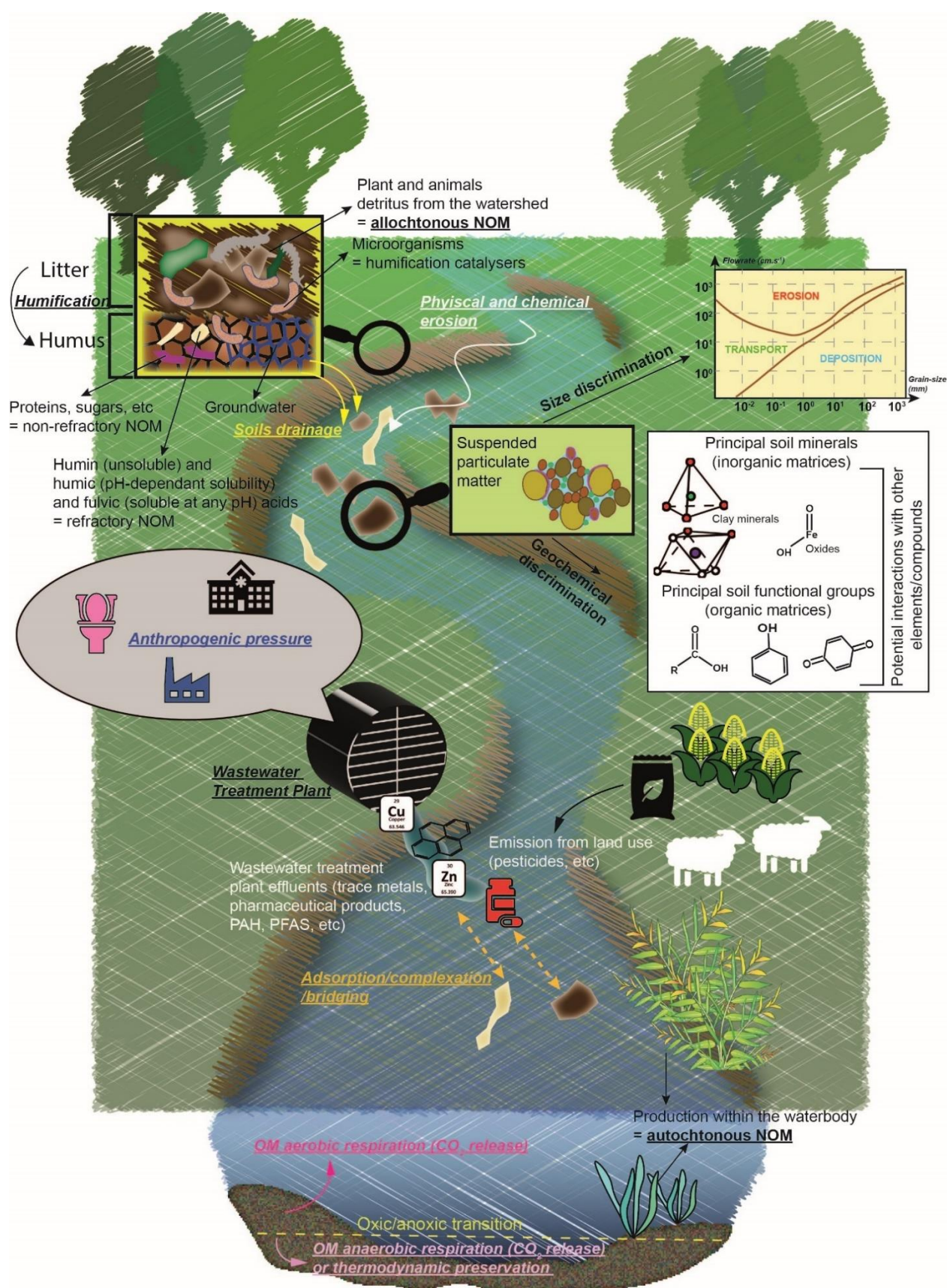


Figure 1. 3: Natural matrices and anthropogenic tracer sources, forms and fate in suburban context. Suspended particulate matters are the result of erosion of soils by stream waters. They can be characterized by their size (Hjulström et al., 1935) or their composition (Beckett and Ranville, 2006; Liu et al., 2020). The emission of anthropogenic tracers into the environment is often attributable to wastewater treatment plants, land-use and industrial activities (cf General Introduction). The fate of these tracers depends on the affinity for the matrices present in the water-sediment continuum, and on the environmental constraints such as physical-chemical conditions. PAH = Polycyclic aromatic hydrocarbons; PFAS = per- and polyfluoroalkyl substances; OM = organic matter. Not to scale.

1. What major natural reactive matrices do we find in suburban water bodies?

The characterization of water in the literature generally considers its concentrations of major and trace elements, carbonates, and dissolved organic matter (DOM). When looking for the fate of anthropogenic tracers in water, DOM is a preferred parameter because of its known ability to interact with contaminants, of both inorganic and organic nature. Many studies have also investigated the geochemical composition of SPMs, known to contribute to carbon cycle (*cf* General Introduction) and whose concentration in streams varies as a function of the intensity of erosion processes (Davide et al., 2003; Viers et al., 2009). The investigated characteristics of SPMs are often its grain-size distribution, and its composition in major elements and trace metals. However, recent studies have also highlighted the need to investigate the origin and composition of reactive matrices such as organic matter (OM) and mineralogical phases, such as clays, especially when considering the fate of anthropogenic tracers in streams (Ramos et al., 2025).

1.1. Organic matter (OM)

The occurrence of OM in streams is ubiquitous, although it is still a challenge to define and characterize it. Many studies have looked for its characteristics in aquatic systems, both in dissolved (Sharp et al., 2006; Bhatnagar and Sillanpää, 2017; Chen et al., 2023; Ning et al., 2025), and particulate forms (Micić et al., 2011). This represents a first distinction of OM diversity, based on size-fractionation. However, the classification of OM can also be proceeded according to its source, molecular weight, solubility, and composition in functional groups (Beckett and Ranville, 2006; Sillanpää, 2014).

1.1.1. Sources of OM in water bodies

OM from natural origin comes from the transformation of the litter into humus. Litter is essentially composed of plant and animal detritus, and the humification process is mainly possible thanks to the action of microorganisms (Sposito, 2008). This process, which takes place in soils, mainly concerns OM from terrestrial origin. OM from aquatic origin results either from the decomposition of plants and algae, or from primary algal production. If the introduction of aquatic OM into water bodies seems obvious, the introduction of terrestrial OM requires other processes. When terrestrial OM is produced within soils, the origin of the OM can be interpreted as the system in which it has been produced. This way, OM from

watershed contribution is referred to as allochthonous whereas OM from waterbody contribution is referred as autochthonous (Beckett and Ranville, 2006).

In suburban context, watercourses are also generally fed from WWTPs effluents. These effluents are responsible for the emission of OM from anthropogenic source in the environment (Imai et al., 2002; Zheng et al., 2024), which originates mainly from human wastes and also from soluble microbial products used in water treatment cycle (Nam and Amy, 2008).

1.1.2. OM composition and typology

There is no universal chemical formula for OM, and OM molecules are often complex structures with relatively long carbon chains. OM from natural origin is essentially composed of micro-organisms, plant residues, and humic substances, the latter accounting for more than 80 % of soil OM (Yang et al., 2024).

Humic substances are supramolecular associations rather than polymers (Figure 1.4), since the individual molecules that make up their composition are generally smaller than 2 kDa (Sposito, 2008). They are resulting from the degradation of biomatter, which corresponds to the matter biologically synthesized and part of living cells, and are generally refractory (Ghabbour and Davies, 2001). One of the most used fractionations of humic substances is based on their solubility, and results in humic acids, soluble at basic pH; fulvic acids, soluble at any pH; and humin, insoluble (Hayes and Swift, 1978; Stevenson, 1994; Ghabbour and Davies, 2001). Their complex structure (Figure 1.4), provides them with many functional groups facilitating their interactions with other stream matrices (Tardy et al., 1977). The principal functional groups of humic substances are carboxyl, phenolic-hydroxyl, alcoholic-hydroxyl, carbonyl, quinone and methoxyl groups (Hayes and Swift, 1978). These functional groups are responsible for their redox activity and phenolic C=O groups in particular are responsible for the electron donor capacity of humic substances, while carboxyl/quinone groups give humic substances their electron acceptor capacity (Yang et al., 2024).

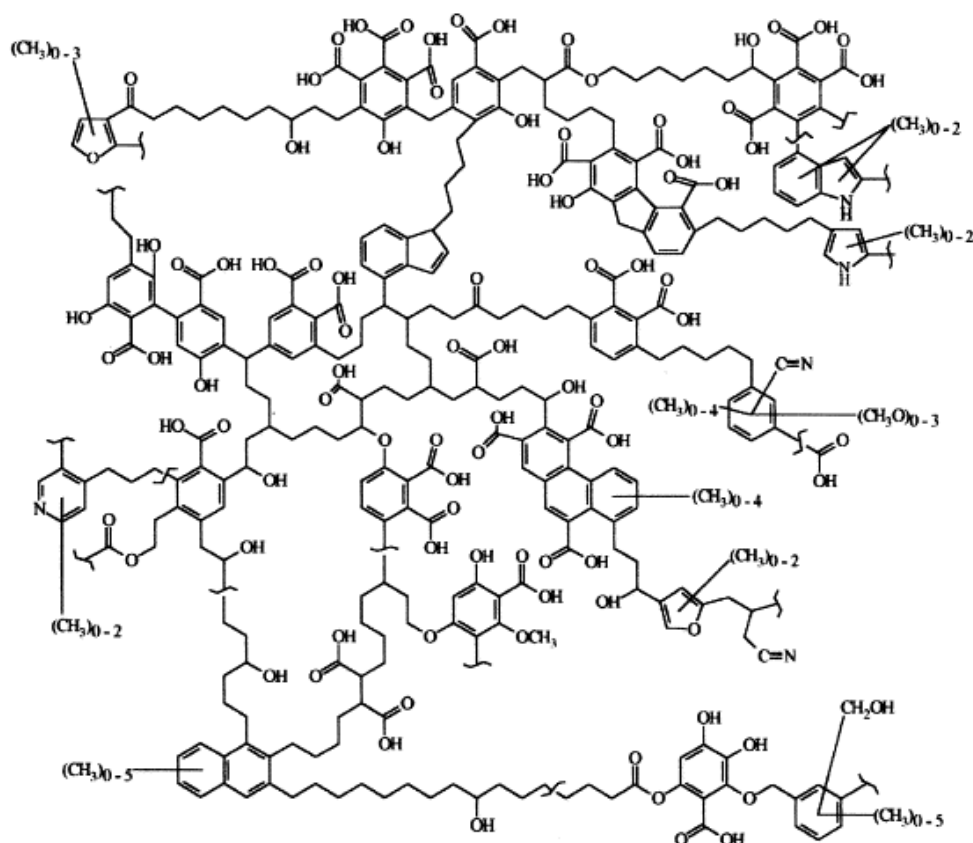


Figure 1. 4: State of the art structural concept of a humic acid. Adapted from Schulten and Schnitzer (1997), Jones and Bryan, (1998).

Compared with humic acids, fulvic acids are more polar and less aromatic, which limits their ability to form hydrophobic interactions. The carboxyl content of fulvic acid is higher than that of humic acids, while their phenolic contents are similar (Sposito, 2008).

Concerning OM from anthropogenic origin, studies usually agree on the differences occurring between OM from WWTPs effluents and natural OM, the latter being more hydrophobic and mostly from terrestrial origin (Nam and Amy, 2008; Quaranta et al., 2012). OM from anthropogenic source, such as found in WWTPs effluents, exhibits characteristics close from those of autochthonous natural OM (Imai et al., 2002; Quaranta et al., 2012), containing proteins, polysaccharides, humic substances and nitrogenous compounds (Yang et al., 2024; Zheng et al., 2024).

1.1.3. OM stability in the natural environment

In the natural environment, OM is exposed to various changing parameters, such as temperature, pH, redox potential and O₂ abundance. Depending on the combination of these parameters, OM will have a different reactivity. Tardy et al. (1997) proposed a calculation of different Gibbs free energies of organic compounds based on their elemental composition,

resulting in their stability diagram with respect to CO₂ and O₂ partial pressures. Also based on the elemental composition of OM, LaRowe and Van Cappellen (2011) evidenced a linear relationship between the Gibbs free energy of a given OM in its standard state and the nominative oxidation state of its carbon. Boye et al. (2017) proposed a thermodynamic interpretation of the NOSC, in both oxic and anoxic environments, with a preferential preservation of OM under anoxic conditions depending on the NOSC value. Redox potential is indeed an important factor in the development of microorganisms, the latter being available in a specific Eh-range, depending on the community (Husson, 2013). Since microorganisms are catalyzers of OM preservation/degradation (Boye et al., 2017), the latter depends on the knowledge of the redox potential, and of its variations.

1.1.4. OM interactions with anthropogenic tracers

The affinity of OM for metals and organic compounds such as pharmaceutical products has been well documented (Lu and Allen, 2002; Maoz and Chefetz, 2010; Ding et al., 2013; Bao et al., 2023). Therefore, its consideration has been progressively included in studies investigating the fate of anthropogenic tracers in the environment (da Silva et al., 2011; Aminot et al., 2015; Al-Khazraji and Boxall, 2016). Metal cations-OM complexes have been particularly studied in the second half of the 20th century (Reuter and Perdue, 1977; Tessier et al., 1980), in a context of river and soil pollutions. The number of studies exploring the interactions between OM and persistent organic pollutants increased as well (Murphy and Zachara, 1995; Kubicki and Apitz, 1999; Nam et al., 2008).

If OM has often been considered in its globality, for example only through OC (particulate and/or dissolved) concentrations (Shafer et al., 1997; Nam et al., 2008), an increasing number of works focused more particularly on its composition in relation with the bounds OM could create with anthropogenic tracers. Carboxyl and hydroxyl groups of OM are the main exchangeable groups, which promotes metal ions sorption (Havelcovà et al., 2009). The sorption of organic hydrophobic compounds to OM is generally driven by the hydrophobic effect (Pignatello, 1998). In the case of ionized compounds, other studies also suggest the occurrence of electrostatic interactions between positively charged organic compounds and negatively charged functional groups of OM (Maoz and Chefetz, 2010). Other possible interactions include cation exchange, van der Waals interactions and bridging complexation, whereby a bond forms between a metal cation and a negatively charged mineral surface via a functional group (Sposito, 2008).

In the natural environment, these interactions might be either enhanced or disadvantaged regarding parameters such as the pH and the ionic strength (Christl, 2012). Indeed, in water bodies, metal ions are in competition with other dissolved species (Pinheiro et al., 2000). Moreover, Zhou et al. (2005) highlighted an enhanced sorption of Ni by humic substances when pH increases. Concerning organic compounds, the pH will also determine the dissociation of the functional groups of both organic matter and organic compounds, influencing their sorption capacity.

1.2. Mineralogical matrices

Mineralogical matrices are a major constituent of soils, accounting for around 45% of their composition. These include mainly calcite, oxides and clays. Clays are particularly reactive mineral structures. Their properties, such as their cation-exchange capacity, allow them to interact with other matrices, including OM, non-natural organic compounds, metals and trace metals. In the context of anthropogenic pressure, clays are used to naturally remove pollutants from aquatic systems (Han et al., 2019; Ewis et al., 2022). They are also used in nuclear waste management. Oxides, such as iron and manganese oxides, are also highly reactive, and likely to interact with trace metals (Tessier et al., 1979) as well as with organic compounds such as pharmaceutical products (Zhao et al., 2017). However, while clays are sensitive to changes in pH, oxides are also highly sensitive to redox changes, making their interactions with other matrices highly variable. The adsorption on clay minerals is known to be stable and efficient, notably due to their high specific surface area, making them excellent carrying phases (Ewis et al., 2022).

1.2.1. Clay minerals structures and characteristics

Clay minerals are aluminosilicates belonging to the clay fraction of soils ($<2\ \mu\text{m}$). They are structured as a composition of tetrahedral and octahedral sheets. The kaolinite group designates clay minerals with a 1:1 layer structure consisting of an alumina octahedral sheet and a silica tetrahedral sheet (Figure 1.5; Theng and Lagaly, 2006; Cheng et al., 2012). This group is known to be the most abundant clay mineral group in soils, and has the generic formula $[\text{Si}_4]\text{Al}_4\text{O}_{10}(\text{OH})_8 \cdot n\text{H}_2\text{O}$ (Sposito, 2008). The two sheets are linked by van der Waals forces and hydrogen bonds (Cheng et al., 2012). The charge of the edges, and therefore the cation-exchange capacity (CEC) of kaolinite, are pH-dependent, which limits its interaction with available cations.

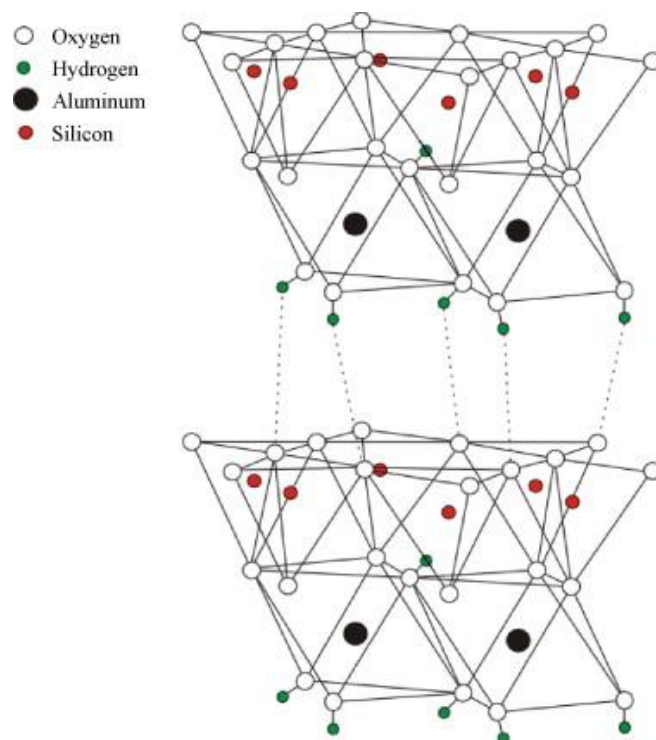


Figure 1. 5: Representation of kaolinite structure, Cheng et al. (2012).

1.2.2. Clay minerals interaction with anthropogenic tracers

The structure and CEC of clay minerals enable them to interact with metal cations and certain organic compounds. Many studies have investigated clay minerals' ability to adsorb either trace metals (Miranda-Trevino and Coles, 2003) and organic compounds such as pharmaceutical products (Figueroa et al., 2004; Thiebault et al., 2020; Chauhan et al., 2020). Kaolinite in particular has become a natural cleaner used in WWTPs processes, due to its affinity for phenols, a widespread functional group of organic compounds (Hounfodji et al., 2021). However, the maximum adsorption capacity of clay minerals, and of kaolinite in particular, is limited, and varies from one molecule to another. Kaolinite structure implies that adsorption at the edges is the dominant interaction, while other clay minerals, such as smectite, also have swelling properties. The edge charges of kaolinite are also pH-dependent (Tofighi and Rahnemaie, 2023), and its surface charges are ionic strength-dependent (Wang and Siu, 2006), which limits the environmental conditions under which the adsorption is likely to occur. As kaolinite is not the only natural reactive matrix in the environment, the competition with other matrices, such as OM must also be considered.

This first section presented the characteristics of the reactive natural matrices found in the water-sediment continuum, likely to interact with anthropogenic tracers. OM is particularly likely to create bonds with anthropogenic tracers thanks to its high number of functional groups, although this matrix appears to be sensitive to physico-chemical conditions such as the redox potential, which drives either its preservation or degradation. Clay minerals such as kaolinite have also been widely investigated for their affinity for anthropogenic tracers, in particular cations. The properties of these two matrices will be particularly examined in the following work, with a particular interest for OM.

2. What tracers do we find in suburban areas under anthropogenic pressure?

As practices evolved, including soil occupation, and the subsequent industrial revolutions, anthropogenic pressures began to affect the environment (Klink and Moreira 2002). These pressures are characterized by multifactorial processes, including increased erosion rates, the higher atmospheric CO₂ level, and the emission of anthropogenic tracers from various origin/sources (Figure 1.6). This era is known as the Anthropocene (Ruddiman, 2013). Scientific and technological advances were driven by the development of industrial activities such as the extraction of rare metals and the refining of petrol. Consumerism has necessitated higher agricultural production, sometimes using pesticides to increase the yields. Thanks to the development of new medications and pharmaceutical products, our life expectancy has increased. These anthropogenic tracers act as our fingerprints. Some of them are moreover highly persistent and dangerous to ecosystems (Ali et al., 2019; González-González et al., 2022).

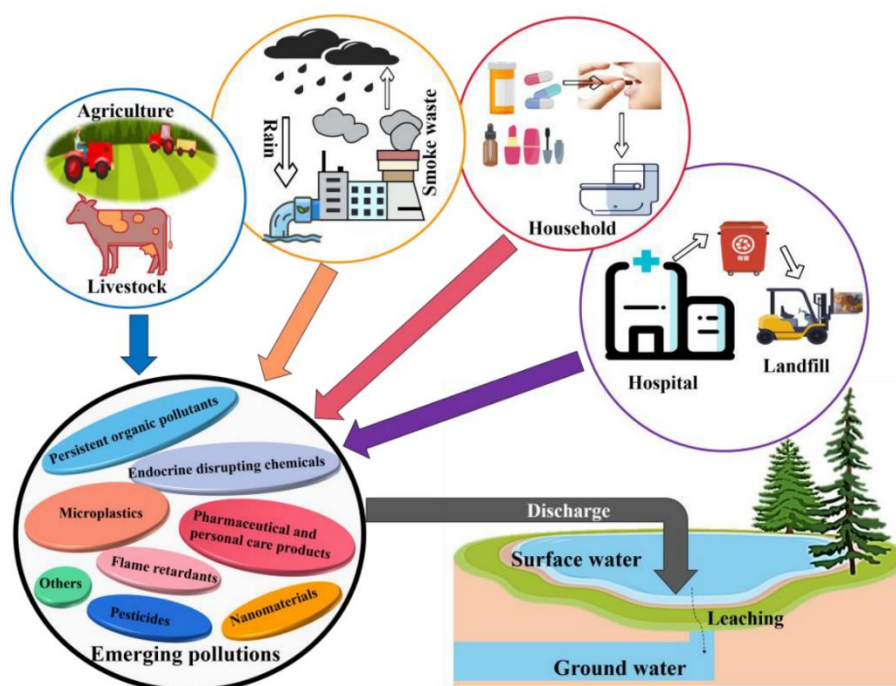


Figure 1. 6: Resource of emerging pollutants and routes to the aquatic system, Dong et al., 2023

2.1. Organic emerging compounds

The presence of persistent organic pollutants (POPs) in the environment can be related to accidental punctual events, but the most concerning form of emission is probably the chronic emission, accompanied by chronic exposure of ecosystems. The Stockholm Convention has therefore listed POPs and has recommended monitoring their occurrence and fate in the environment (Mbengue, 2001). This is the case with pharmaceutical products (PPs), which are consumed worldwide and continuously. There are more than 6000 PPs on the market (French Pharmacology Academy, Avis Prop. loi Pénuries, 2024) including more than 3000 active substances for humans and animals, representing over 100 000 tonnes of PPs per year (Medication and Environment Report, French Pharmacology Academy, 2019).

The impact of pharmaceutical products on the environment is a concern because the aim of medication is to act on targets, that are also part of ecosystems. When ingested, and then emitted into the environment, PPs are neither fully metabolized nor fully biodegraded, which makes them persistent (Heberer et al., 2002). Their half-life varies greatly between different molecules, ranging from days to months (Andreozzi et al., 2003).

There are many therapeutic categories of PPs, including antibiotics, beta-blockers, pain-killers, cancer treatments, antidepressants and hormones. Consumption rates vary around the world due to differing levels of accessibility in different countries, as well as over

time (Wilkinson et al., 2022). Apart from their use, PPs can also be classified according to persistence, biodegradability, and physico-chemical characteristics. This highlights the complexity of surveying PPs in the environment, since each molecule has its own intrinsic properties.

2.1.1. PPs in the environment: why and when did concern start to be raised?

Concern about the occurrence and the fate of PPs in the environment began to grow from the second half of the 20th century onwards. The first identification of PPs in the water was made by Hignite and Azarnoff (1977) (Medication and Environment Report, French Pharmacology Academy, 2019). Often present at trace or ultra-trace levels in the environmental matrices, PPs have been the subject of particular study following technological improvement in quantification methods. The development of extraction procedure and quantification using LC-MS/MS has enabled the investigation of PPs at concentrations as low as ~1 ng/L. However, these advances were not the only factors behind the increase in studies of PPs in the literature. Indeed, while a significant proportion of studies have focused on their occurrence, others have also highlighted their potential toxic effects on ecosystems, even at low concentrations, (Hernando et al., 2006), since they are not fully metabolized in the human body. Halling-Sorensen (1998) presented two phases of PPs transformation within an organism: the first characterized by oxidation, reduction and/or hydrolysis of the parent molecule; and the second, called conjugation, which is supposed to render the molecule inactive. This means that the PPs formed after being emitted into the environment may be either parent molecules or metabolites (Patel et al., 2019). Nevertheless, few studies have examined the metabolites and degradation products of PPs and of organic compounds in general (Heberer, 2002; French Pharmacology Academy 2019), despite the fact that these may be more toxic (Halling-Sorensen, 1998; Isidori et al., 2005). Fishes are especially sensitive to active compounds, and are threatened by hormones while bacteria are likely to develop resistance to antibiotics.

In order to overcome these environmental threats, the beginning of the 21st century witnessed the creation of associations and Non-Governmental Organizations (NGOs) worldwide, with plans dedicated to surveying PPs, establishing environmental norms concerning their concentrations in aquatic systems and determining risk thresholds. While concerns had already begun years earlier, 2015-2016 seemed to be a particularly transitional year. Indeed, PPs residues were included in the French Micropollutants Plan (MEEM, 2016),

and antibiotics were added to the list of the EU Commission Decision 495/2015 (Barbosa et al., 2016). The first edition of the ICRAPHE Conference (International conference on risk assessment of pharmaceuticals in the environment), which took place in Paris in 2016 (French Pharmacology Academy, 2019) is a good example of national concern.

2.1.2. The arrival of PPs in the aquatic system: where do they come from?

PPs have different consumption, and therefore emission rates. Consumption rates highly depend on the country being studied, as well as on the availability of medication, healthcare priorities and needs. Emission rates, on the other hand, depend on water treatment plants efficiency and technology, which vary a lot around the world. Wilkinson et al. (2022) published a global study on the occurrence of PPs in rivers. It appeared that the most contaminated samples were mainly from Africa, and, in general, from low- to middle-income countries with little awareness of PPs pollution, due to the small number studies on the subject. Carbamazepine, metformin and sulfamethoxazole were among the most frequently detected PPs, which is consistent with other studies on surface waters (Luo et al., 2014), with detection frequencies ranging from 40 to 60 %.

Understandably, concentration rates are the highest when samples are collected directly from the outlet of wastewater treatment plants (WWTPs), which are their main emission pathways (Jacob et al., 2020; Ledieu et al., 2021; Thiebault et al., 2021). Indeed, the diverse characteristics of PPs make their removal from WWTPs effluents challenging. The removal rate is likely influenced by both wastewater characteristics and operating conditions, as well as PPs properties (Patel et al., 2019; Chavoshani et al., 2020).

PPs are also often quantified in stream water downstream of WWTPs, in order to evaluate the attenuation of their concentrations (Roberts and Thomas, 2005). This may result from dilution by the natural stream, which is difficult to evaluate, since it depends on the hydrological regime and extreme rainfall or dryness events. The decrease in PPs concentration in the dissolved phase may also be due to their transformation or degradation by environmental factors, such as photolysis or adsorption onto particulate matters (Perez et al., 2022).

2.1.3. PPs fate in the aquatic system: a non-unique pathway?

The fate of PPs, once they are emitted into the environment has also raised concern, since their bioavailability and toxicity depend on the form and the pathways they follow in the aquatic environment (Figure 1.7). Non-persistent or easily degradable PPs undergo various forms of transformation and degradation in stream water, including photodegradation,

biotransformation (microbial degradation and phytodegradation) and sorption (Andreozzi et al., 2003; Kunkel and Radke, 2012; Rühmland et al., 2015; Rodriguez-Lopez et al., 2022). The rate of these processes depends on both the characteristics of the PPs and environmental factors including light intensity, microbial communities, the availability of carrying matrices and water physico-chemical properties.

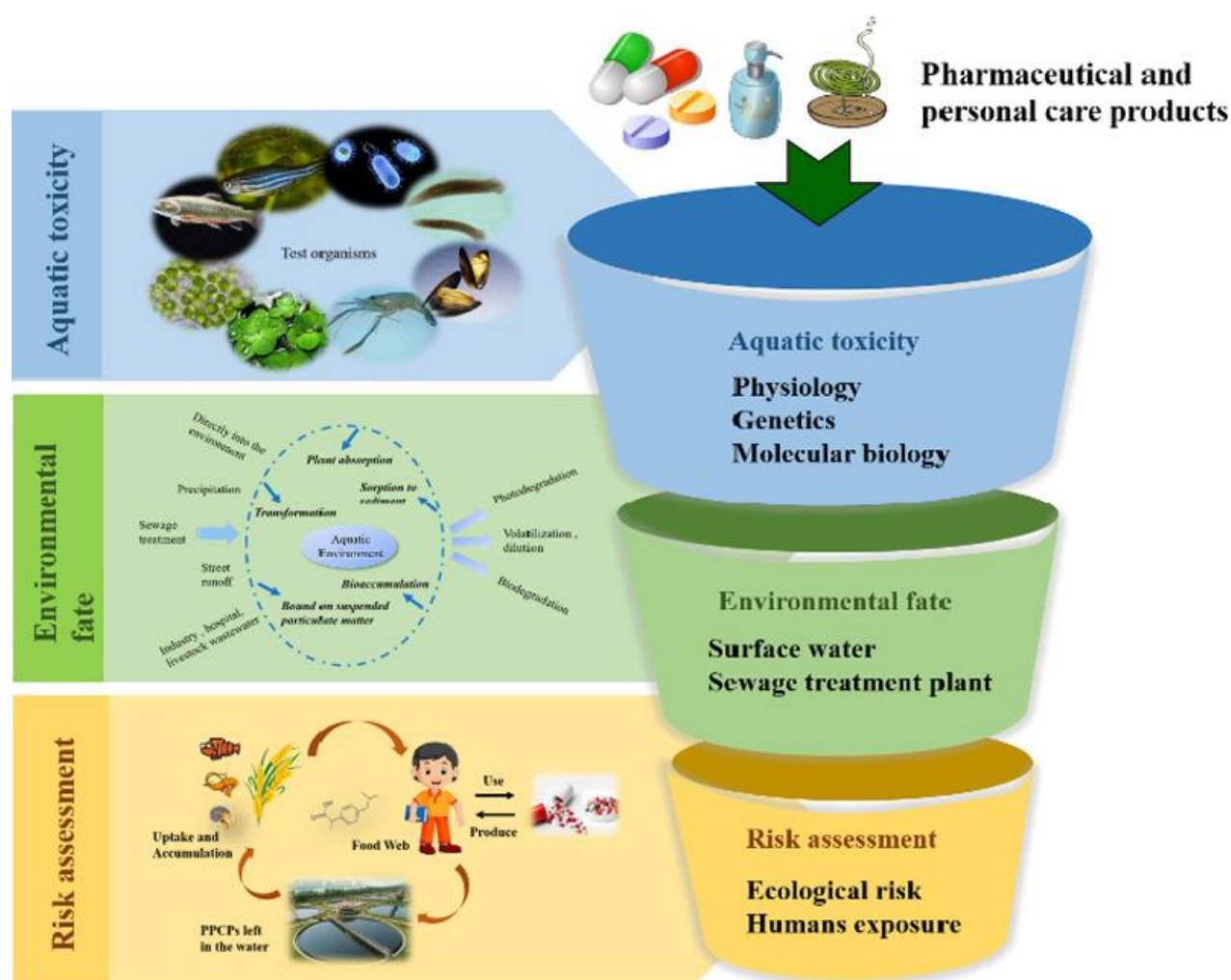


Figure 1. 7: Risk assessment, environmental fate and aquatic toxicity of pharmaceutical and personal care products, Wang et al., 2021.

The distribution of PPs in the water-sediment continuum relates to their occurrence within various matrices, such as water, suspended particulate matters (SPMs) and sediments. While the quantification of PPs in the aqueous fraction has been particularly studied in the literature (Robert and Thomas, 2006; Bound and Voulvoulis, 2006; Kunkel and Radke, 2012; Wilkinson et al., 2022), an increasing number of papers also address their presence in solid matrices, especially SPMs (Hernando et al., 2006; Lahti and Oikari, 2011; Boulard et al., 2020). The properties of PPs, such as their octanol-water partition coefficient (K_{ow}), their

dissociation constant (pKa) determine whether they are hydrophilic or hydrophobic, and their dissociation in water, giving their polarity, respectively. The affinity of PPs for organic matter has been also investigated, although the precise interactions and bonding between organic matter and PPs' functional groups remain relatively little studied. Indeed, these precise interactions are most of the time investigated in mechanistic studies (Pignatello, 1998; Yamamoto et al., 2003), but in studies investigating a specific area, with an environmental survey, OM is often considered through the single TOC value (Nam et al., 2008; Ledieu et al., 2021).

Another important characteristic of PPs is their half-life, which varies greatly between molecules and depends on the composition of the carrying matrix, for example in humic substances (Andreozzi et al., 2003). Some molecules, such as carbamazepine, exhibit high persistence in the environment, and are even therefore used to trace WWTPs effluents (Boulard et al., 2020). In general, the fate of PPs in the environment is difficult to comprehend, due to the high variability in PPs characteristics (Table 1.1), and the differences in environmental parameters.

The fate of PPs also depends on that of their carrying matrices. Indeed, SPMs are transported by streams through the watershed until they reach an outlet; sometimes this is a retention area. As flow decreases at the outlet, SPMs are likely to settle, as are the sorbed PPs. Diagenesis mechanisms are then related to the geometry of the retention area and its specific physical and chemical properties within the water-column. Only a few studies have investigated the behavior of PPs in retention areas (Larà-Martin et al., 2015; Schimmelpfennig et al., 2016), while this particular environment is likely to raise the question of the stability of their sorption.

This section presented the origins of the growing interest for PPs fate in the water-sediment continuum. It allowed to identify their main source, which is WWTPs effluents and highlighted the variety of their pathways in the natural environment, regarding both their intrinsic properties, as well as the properties of the matrices belonging to the water-sediment continuum. The following work therefore questions the nature of the affinity of PPs for the reactive matrices of the particulate phase, as well as the preservation/degradation of this particulate phase, especially when it is accumulated within retention areas, and finally explores the stability and eventual reversibility of PPs trapping onto the particulate phase (Figure 1.8).

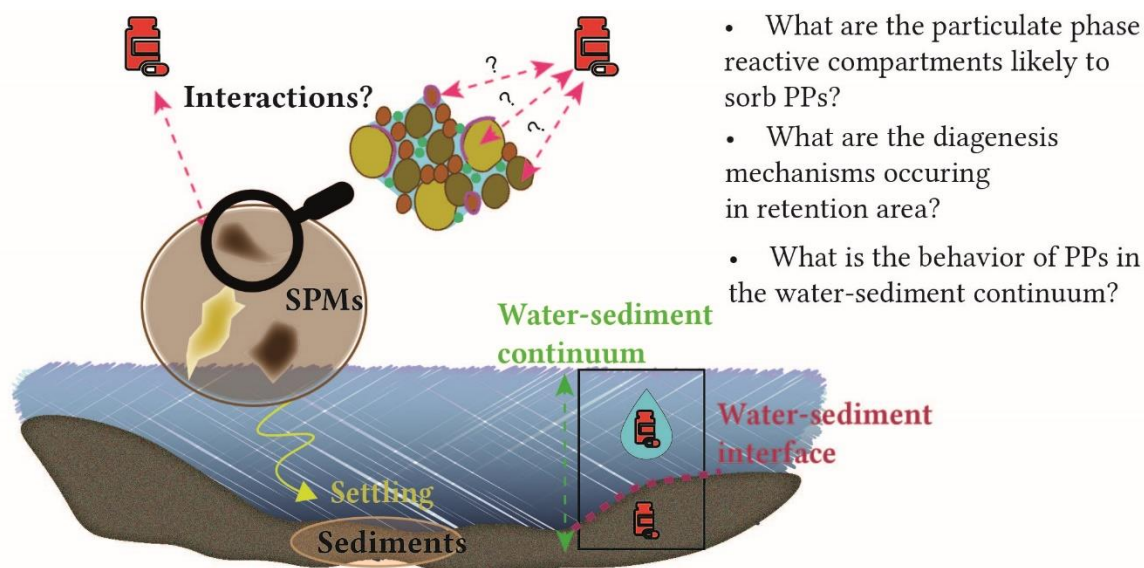


Figure 1. 8: Main scientific issues explored in the present study, including the determination of pharmaceutical products (PPs) carrying phases, the investigation of carrying phases preservation/degradation in the context of their accumulation in retention areas, and the stability and potential reversibility of PPs trapping by their carrying matrices.

The following thesis focuses on the fate of 10 PPs, that are carbamazepine (CBZ), oxazepam (OXA), diazepam (DIA), paracetamol (PAR), tramadol (TRA), atenolol (ATE), fluoxetine (FLX), venlafaxine (VFX), metoprolol (MTP) and diclofenac (DIC). These PPs are emitted through WWTPs effluents and have been quantified in the water-sediment continuum. Some of them reached concentrations of great concern (Ledieu et al., 2021). Furthermore, they exhibit different physico-chemical characteristics, in terms of charge and of lipophilicity/hydrophilicity (Table 1.1), potentially related to different pathways in the environment. These PPs were quantified in surface sediments and in pond water, both collected at the water/sediment interface, using liquid-chromatography coupled with tandem mass-spectrometers (LC-MS/MS). Their respective limits of detection and quantification are given in the Appendixes of Chapter 3, 4 and 5. In these three Chapters, PPs will be mainly classified following their main form in the natural waters (neutral/cationic/anionic).

Table 1. 1: Physical-chemical and environmental characteristics of 10 PPs. MW = Molecular Weight (g.mol^{-1}). ^aThiebault et al., 2017 ; ^bdrugbank.ca.

Pharmaceutical Products	Abbreviation	Chemical formula	Therapeutic class	$\text{pK}_a^{\text{a,b}}$	Main form at pH 7	$\text{Log (K}_{\text{ow}})^{\text{a,b}}$	$\text{Log (K}_{\text{oc}})^{\text{a,b}}$	MW (g.mol^{-1}) ^{a,b}
Carbamazepine	CBZ	$\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$	Antiepileptic	2.3 and 13.9	Neutral	2.45	3.56	236.27
Oxazepam	OXA	$\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2\text{Cl}$	Anxiolytic	1.7 and 11.6	Neutral	3.34	3.08	286.71
Diazepam	DIA	$\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{O}$	Anxiolytic (tranquilizer)	3.4	Neutral	2.70	4.05	284.74
Paracetamol	PAR	$\text{C}_8\text{H}_9\text{NO}_2$	Analgesic/antipyretic	9.6	Neutral	0.46	1.79	151.16
Tramadol	TRA	$\text{C}_{16}\text{H}_{25}\text{NO}_2$	Analgesic	9.4	Cationic	3.01	2.91	263.37
Atenolol	ATE	$\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_3$	Beta-blocker	9.6	Cationic	0.16	3.56	266.34
Fluoxetine	FLX	$\text{C}_{17}\text{H}_{18}\text{F}_3\text{NO}$	Psychotropic	9.8	Cationic	4.65	5.32	309.33
Venlafaxine	VFX	$\text{C}_{17}\text{H}_{27}\text{NO}_2$	Psychotropic	8.9	Cationic	3.28	3.17	277.4
Metoprolol	MTP	$\text{C}_{15}\text{H}_{25}\text{NO}_3$	Beta-blocker	9.7 and 14.1	Cationic	1.79	2.75	267.36
Diclofenac	DIC	$\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{NO}_2$	Anti-inflammatory	4.2	Anionic	4.02	2.92	296.15

2.1.4. Investigated areas: what about site-specificities?

The occurrence of organic pollutants, primarily PPs, has been observed worldwide. (Patel et al., 2019; Wilkinson et al., 2022). Studies investigating the behaviour and transfer of PPs in the environment have been performed in both “large-scale” and “small-scale” catchments (>100 km² and 5-10 km², respectively, Moldan and Cerny, 1994; Latron and Lana-Renault, 2018). Several compartments have been sampled in this purpose, including WWTPs effluents, stream water downstream WWTPs, SPMs and accumulated sediments, sometimes simultaneously (da Silva et al., 2011; Aminot et al., 2015; Paiga et al., 2016; Ledieu et al., 2021). Inter-comparison has been difficult to interpret due to differences between the catchments, including their sizes, the flow rates of river and tributaries, the number of tributaries and WWTPs, the flow rates of WWTPs effluents as well as their corresponding equivalent populations (EP). However, the following schematic literature review performed on 9 watersheds, all exhibiting different geomorphological and hydrological characteristics (Figure 1.9), has revealed concentrations of PPs, in both dissolved and particulate phases, reaching similar orders of magnitude, whatever the investigated compartment (WWTPs effluents, stream water, SPMs, sediments). This highlights the considerable sensitivity of small-scale catchments to this pollution. Indeed, streams in small-scale catchments generally present lower flow rates, which results in a lower dilution of WWTPs effluents and consequently a higher exposure of ecosystems.

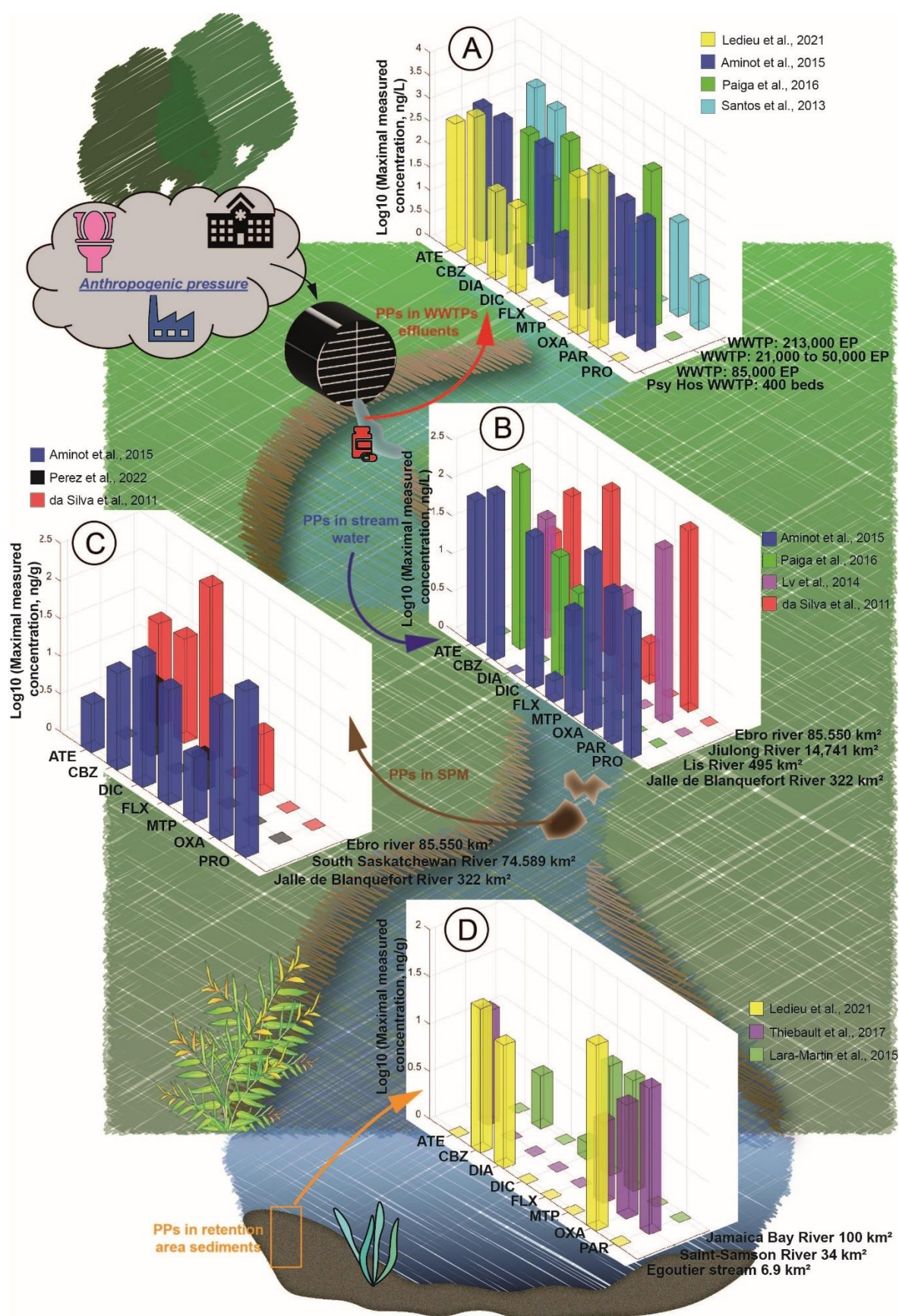


Figure 1. 9: Histograms representing the maximal, or mean maximal, concentrations of PPs (logarithmic scale, ng/g or ng/L) in the effluents of WWTPs (A), in the dissolved phase of river waters downstream WWTPs (B), in the particulate phase of river waters downstream (C), and in sediments accumulated within retention areas (D). WWTPs = Wastewater treatment plants; Psy Hos = psychiatric hospital; EP = equivalent population. PRO = Propranolol. Not to scale.

This last section demonstrated the potential of small-sized watershed to exhibit concentrations in PPs of great concern, both under dissolved and particulate phases. It moreover demonstrated the potential of retention areas to constitute hotspot of PPs by the accumulation of particles being themselves carriers of PPs.

The following work will therefore investigate the behaviour of the 11 PPs presented hereinabove in the water-sediment continuum, at the scale of the Beulie pond, located in the Egoutier watershed (Semoy, Loiret France). This work complete previous studies that investigated the transfer of SPMs from source (soils) to their (partial) sink (the Beulie pond, Ledieu et al., 2020)), as well as the sources of PPs emitted quantified in SPMs and Beulie pond surface sediment (Ledieu et al., 2021, Figure 1.10).

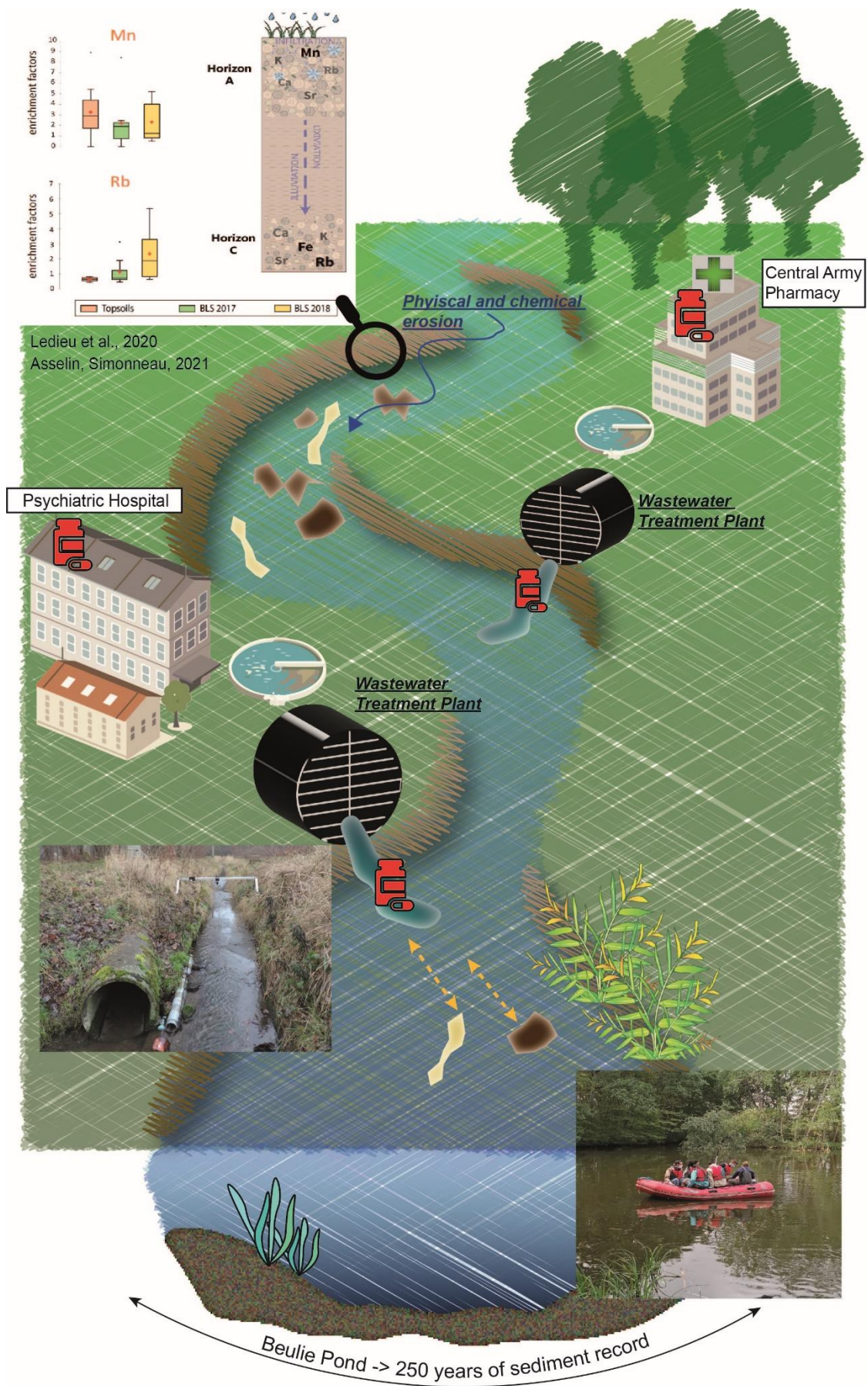


Figure 1. 10: Natural matrices and pharmaceutical products sources in the Egoutier catchment. Not to scale.

Chapter 2. Study area, scientific approach and analytical and experimental strategies



1. Pharmaceutical product fates in the environment: what would be the characteristics of a relevant study area?

Pharmaceutical products (PPs) fate in the environment has been investigated in many studies, particularly these last decades, associated with an increasing concern about water good ecological state (*cf* Chapter 1, references included). However, as far as we learned from the literature, apart from the occurrence of PPs in waterbodies, the characteristics of the studied areas, in terms of hydrology, geochemistry and geomorphology are little discussed, while these factors might have an influence on contaminants behaviour (Smolyakov et al., 2010; Manamsa et al., 2016). Indeed, the hydrology of catchments drives water flow rate, which controls erosion rates and thus the availability in suspended particulate phases, and also the dilution rates of WWTPs effluents usually bringing PPs into the natural environment (*cf* Chapter 1, references included). The geochemical composition of the aqueous and particulate phases is also often scarcely described, while it is directly linked with the affinity of PPs for either the aqueous or the particulate phase. Organic matter (OM) characterisation is typically often limited to the Total Organic Carbon (TOC) content quantification, which hides the role played by OM most reactive fractions. Physico-chemical parameters such as the pH controls PPs charge in the natural environment as well as the charge of available adsorption sites such as clay edges, and thus the electrostatic interactions likely to bind PPs onto particles. The ionic strength has also been found to influence the adsorption capacity of the solid phase (Gao and Pedersen, 2005), and the redox potential is likely to affect the degradation and/or preservation of OM, and thus its functionalization which controls the bounds it might create with PPs. However, these parameters are still frequently missing from studies. Catchments typology, including their size and connectivity between waterbodies is also scarcely discussed, while small-sized watersheds in particular are known to exhibit more rapid response to extreme hydrological events. Furthermore, catchments including retention areas promote the sedimentation of particles, which limits their transfer in the natural environment. When particles are moreover carrying PPs, retention area can act as hotspots of PPs (Figure 2.1 A). PPs transferred in the environment are often subjected to geochemical contrasts, like changes in pH between the stream and the retention area for example. Furthermore, natural matrices likely to create bonds with PPs, such as OM, can also have different dissolved and particulate concentration, forms and degradation state along catchments, which questions the durability of its affinity for PPs, and thus the fate of PPs over long distance (Figure 2.1 B).

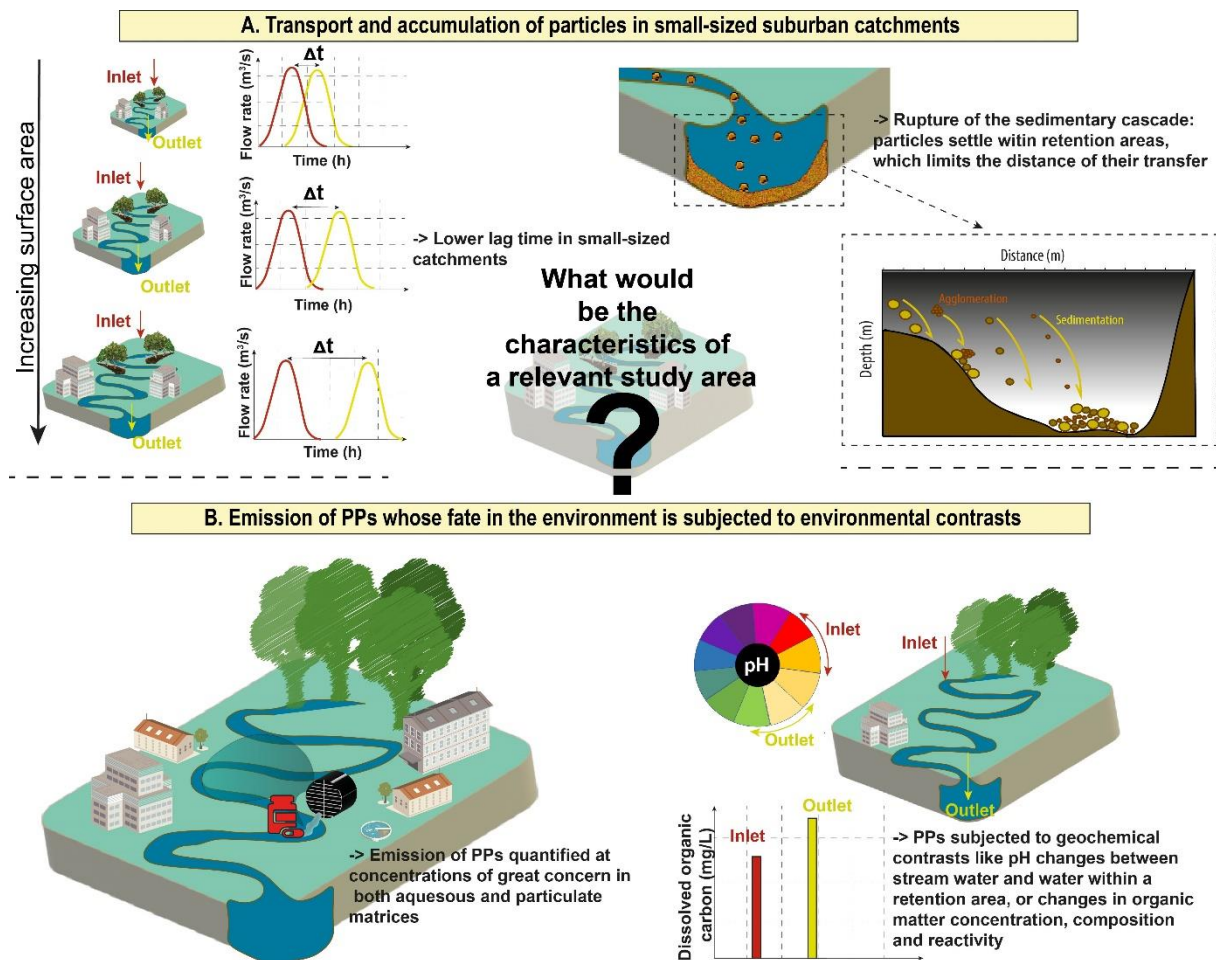


Figure 2. 1: Characteristics of a relevant study area in the context of pharmaceutical product fate in the environment: A. Small-sized watershed are characterized by a higher sensitivity and a more rapid response to hydrological events which influence the availability in suspended particulate matter and control their transfer while retention areas promote the sedimentation of particles, which limits the distance of their transfer. B. Pharmaceutical products (PPs) can be subjected to geochemical contrasts, like changes in pH between the stream and the retention area for example, or OM concentration, composition and reactivity along the catchment.

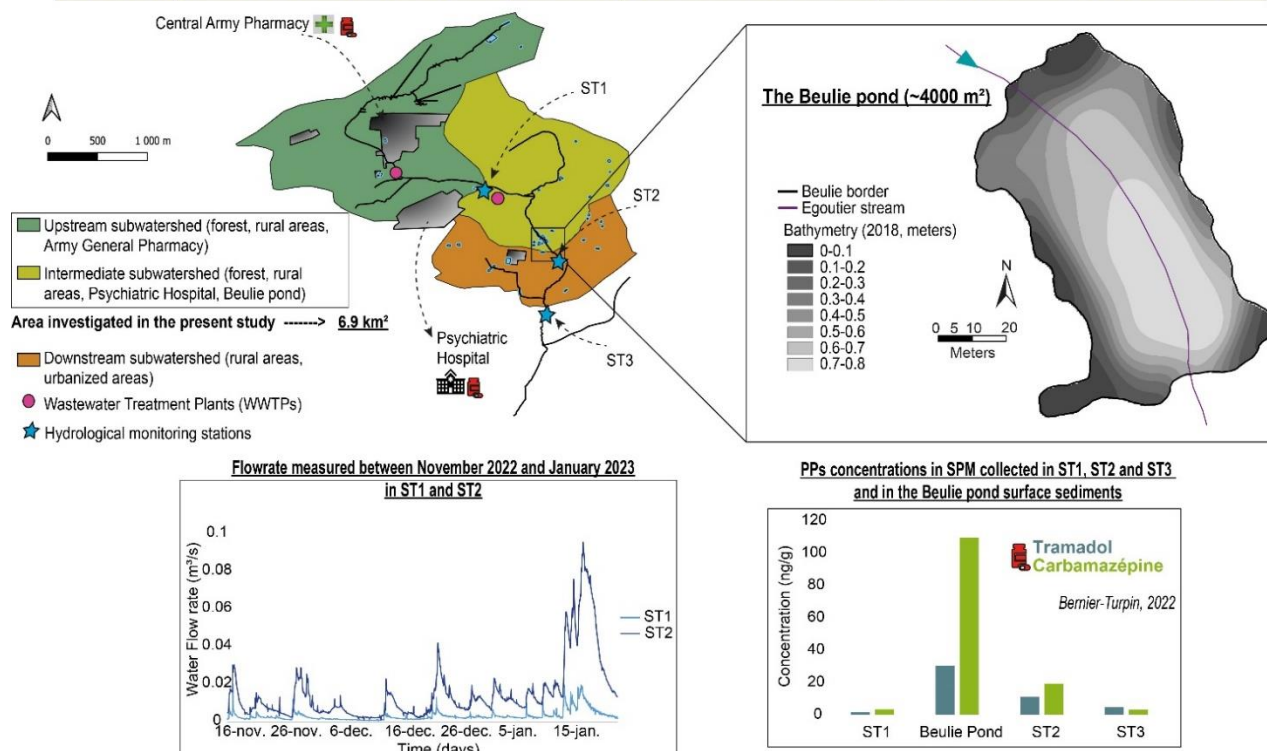
2. The Egoutier catchment: what makes this study area a relevant one?

The Egoutier catchment is located in the North-East of Orléans, in Semoy (Loiret France) and drains a total area of 27 km², but the present study investigates an area of 6.9 km², whose outlet is the Beulie pond, a retention area of about 4000 m². It is characterized by an upstream/downstream gradient of anthropogenic pressure, characterized notably by the emission of PPs through the effluents of two WWTPs, one belonging to the Central Army Pharmacy and the other one belonging to a psychiatric hospital (Ledieu et al., 2021). The catchment has been instrumented in 2018, and therefore comprises 3 hydrological survey stations, namely ST1, ST2 and ST3 (Figure 2.2 A). These stations register the water elevation thanks to ultrasound sensors, and the water turbidity with nephelometric sensors. ST1 and ST2 also possess rain gauges. The flow rate is calculated from the water elevation continuous measurement and from flow punctual brine gauging measurements that allowed the obtention of a gauging curve.

The flowrate measurements between stations ST1 and ST2 highlighted a synchronous response of both stations to extreme rainfall events, which is a characteristic of reactive catchments (Figure 2.2 A). PPs quantification in SPMs collected in ST1, ST2 and ST3 and in the Beulie pond surface sediments, performed by Bernier Turpin (2022), indicates a preferential accumulation of PPs in the pond surface sediments (Figure 2.2 A). Geochemical analysis and physico-chemical measurements performed along the Egoutier stream showed spatial variability of dissolved organic carbon (DOC) concentrations, the latter being higher right after the inlet of the psychiatric hospital WWTPs and around the Beulie pond. The pH presented also a spatial variability, completed by a temporal variability depending on the seasonality. The evaluation of the degradation state of OM, quantified in soils, SPMs and surface sediments clearly highlighted 3 different trends, with the surface sediments having a degradation state differing from soils and SPMs, while these two compartments are the source of sediments. (Figure 2.2 B). The PhD work of Ledieu (2020) was partially dedicated to the identification of PPs sources in the Egoutier catchment, and the highest contribution was the one of the psychiatric hospital WWTPs effluents, exhibiting concentration in the dissolved phase comparable with concentrations already measured in other studies investigating bigger scale catchment (Figure 2.2 B and Chapter 1).

These measurements, characterizations and analysis, performed from 2018 to now, allowed to support the relevance of the Egoutier catchment as a study area for the investigation of PPs behavior in the water-sediment continuum.

A. The Egoutier catchment and the Beulie pond: transport and accumulation of particles in a small-sized watershed



B. The Egoutier catchment: emission of PPs whose fate in the environment is subjected to geochemical contrasts

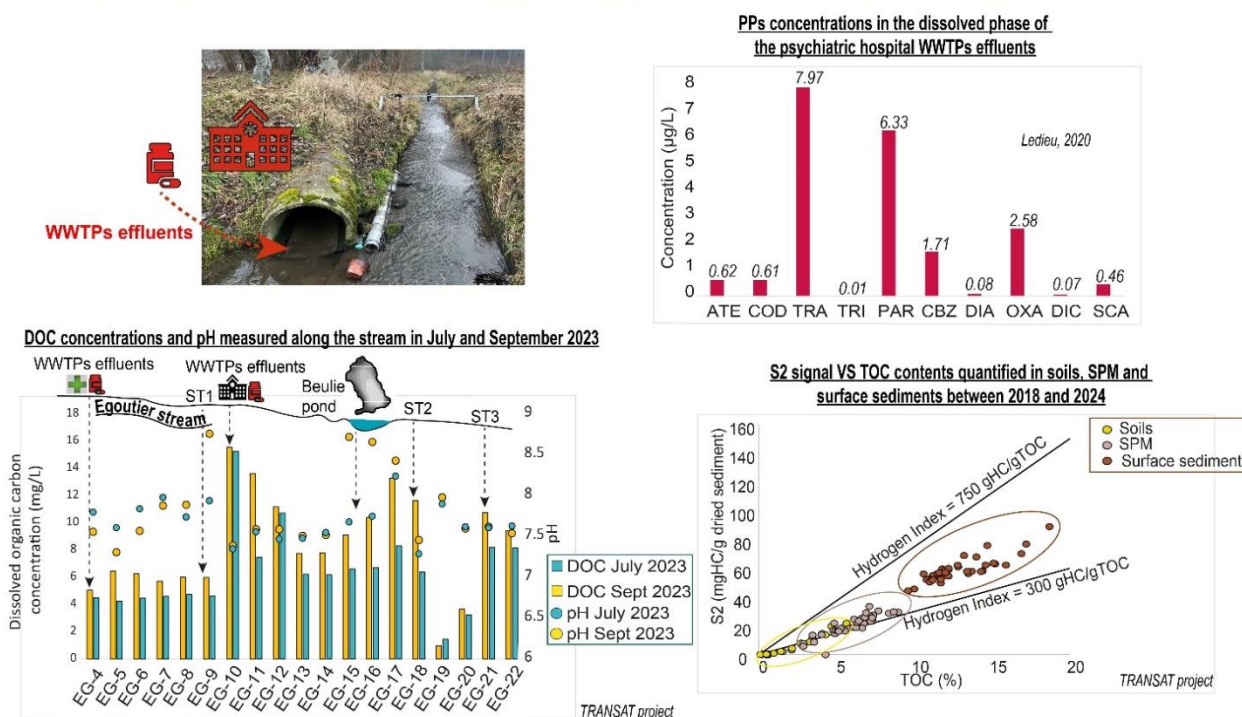


Figure 2. 2: Characteristics of the Egoutier catchment and the Beulie pond as relevant study areas: A. The hydrological survey of the Egoutier stream revealed instantaneous responses between the 2 hydrological stations ST1 and ST2. Furthermore, concentrations measured in particulate phase upstream, within and downstream the Beulie pond highlighted it as a hotspot of PPs. B. PPs were quantified in the dissolved phase at concentration of great concern. Moreover, the measurement of pH along the stream showed more alkaline conditions in the Beulie pond compared with the stream. Finally, organic matter concentration fluctuated in the dissolved phase, while the particulate organic matter was found to have different concentrations between soils, suspended materials and sediment, as well as a different freshness.

3. The TRANSAT Project: what is the contribution of the present study?

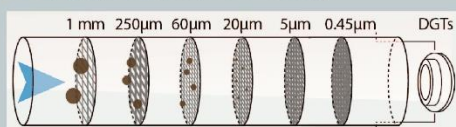
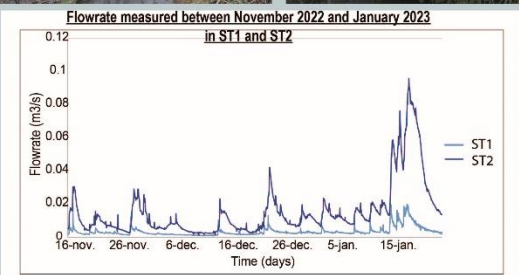
In the context of the preservation of soils and waterbodies good ecological state, the TRANSAT “Transfert particulaire des contaminants en bassin versant anthropisés” (Contaminant particulate transfers in anthropised watersheds) project, founded by the Region-Centre-Val-de-Loire and led by Anaëlle Simonneau, supported the present thesis.

This project followed on from the MOSAIC “Quantification et modélisation des flux sédimentaires actuels et passés à l’échelle des petits bassins versants” (Quantification and modelling of current and past sedimentary streams at the scale of small catchments) APR IA project also led by Anaëlle Simonneau, as well as the PhD work of Lauriane Ledieu.

The TRANSAT project particularly aimed to improve the determination of the transfer of organic micropollutants, such as PPs, in catchments submitted to an anthropogenic pressure. These micropollutants are targeted in the water-sediment continuum, which implies to characterize both aqueous and particulate streams (MOSAIC project). In order to do so, new devices were used, such as the GEACOS sediment traps (Simonneau, 2020), installed at the three monitored stations of the Egoutier watershed: ST1, ST2 and ST3, to collect SPMs. New methodologies were also deployed, such as the quantification of PPs contents both in bed load sediments and water from the Egoutier stream and from the Beulie pond (Thiebault, 2021).

The present PhD thesis is part of the TRANSAT project and investigates the behaviour of PPs in the water-sediment continuum through sediment accumulation in the Beulie pond which has been identified by Ledieu (2020) as a contamination hotspot. It therefore raises the question of the potential reversibility of PPs trapping within surface sediments in the pond, in regard with sediment diagenesis and the physico-chemical characteristics of the water-column (Figure 2.3).

WP1. Particulate phase transport at the Egoutier catchment scale



GEACOS (GranulomEtric pAssive Capture of dissOLved matter & Sediment)
(Simonneau et al., 2020; Dabrin et al., ICOTTE 2023)

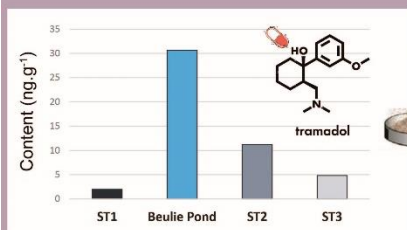
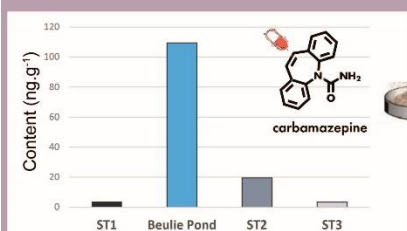


DGTs = diffusive gradient in thin film

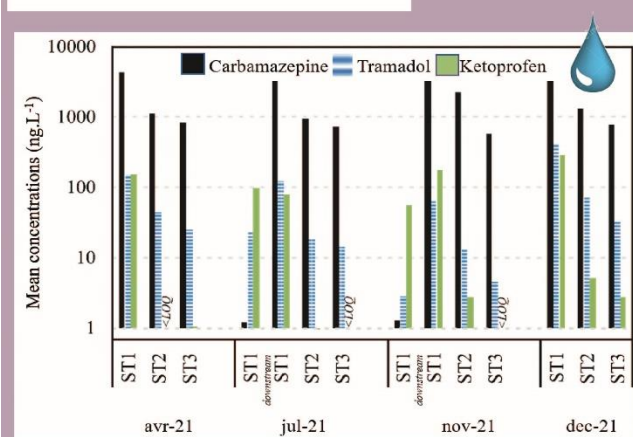
- What are the effects of land use artificialization on erosion processes?
- What are the effects of seasonality on SPM and contaminant transport?

WP2. Pharmaceutical products transfer at the Egoutier catchment scale

(Thiebault, Simonneau, 2021
Bernier-Turpin, 2022)



- What are the factors controlling the transfer of pharmaceutical products in the dissolved and particulate fractions at the Egoutier catchment scale?



The present study

WP3. Fate of pharmaceutical products in the water sediment continuum at the Beulie pond scale?



- What are the particulate phase reactive compartments likely to sorb PPs?

- What are the diagenesis mechanisms occurring in retention area?

- What is the behavior of PPs in the water-sediment continuum?

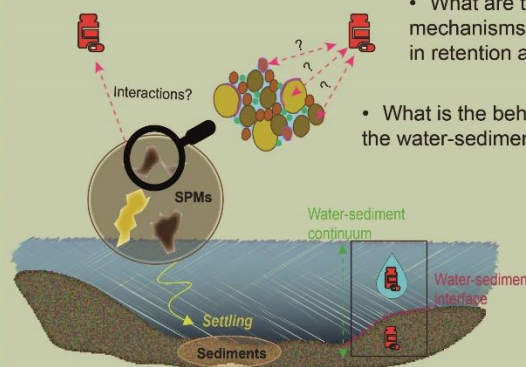


Figure 2. 3: Presentation of the main work-packages part of the TRANSAT project, including the contribution of the present PhD thesis work. Simonneau et al., 2020; Dabrin et al., ICOTTE 2023; Veselská et al., 2025.

4. Which compartments of the water/sediment continuum are part of particulate phase transport and accumulation?

This study is focused on the water-sediment continuum. “Water” refers to the dissolved fraction $<0.45\ \mu\text{m}$, including the colloidal (3.5 kDa- $0.45\ \mu\text{m}$) fraction, and “sediment” refers here to the particulate phase which can be subdivided into two compartments: suspended particulate matters (SPMs), transported by the Egoutier stream, and water/sediment interface surface sediments, that correspond to the few centimetres (around 10 cm thick) recently accumulated into the Beulie pond.

4.1. The aqueous phase (i.e. filtered under $0.45\ \mu\text{m}$)

Water has been analysed both into the Egoutier stream and within the water column of the Beulie pond. This section will present the sampling strategy employed for both the aqueous phase of the stream and of the pond. The aqueous phase of the pond will be more particularly investigated in the present study since it takes part in pond’s dynamics and in the fate of PPs in retention areas.

The Egoutier stream sampling campaigns occur three times a year, in order to integrate the main seasonal transitions: winter to spring (sampling in March-April), spring to summer (sampling in July) and summer to autumn (sampling in September-October). 21 sampling stations are distributed along the stream (Figure 2.4), and are localised in order to monitor both water bodies connections (new inlets for instance) and soil occupation changes along the upstream/downstream gradient of the watershed.

Water has been collected in High density polyethylene (HDPE) bottles, previously rinsed 3 times with the stream water. It was then filtered at $0.45\ \mu\text{m}$ to remove microorganisms and particles, conditioned in Polytetrafluoroethylene (PTFE) tubes, and stored at $4\ ^\circ\text{C}$ once back in the lab.

The Beulie pond water samples were collected at the water/sediment interface of 3 specific locations within the pond: the delta, the upstream/shallow area and the main decantation basin. These areas were selected regarding the pond’s bathymetric map (Figure 2.4), as it will be discussed in Chapter 3. These areas were reached using a Zodiac® boat. Beulie pond water samples conditioning followed the same procedure than stream water samples.

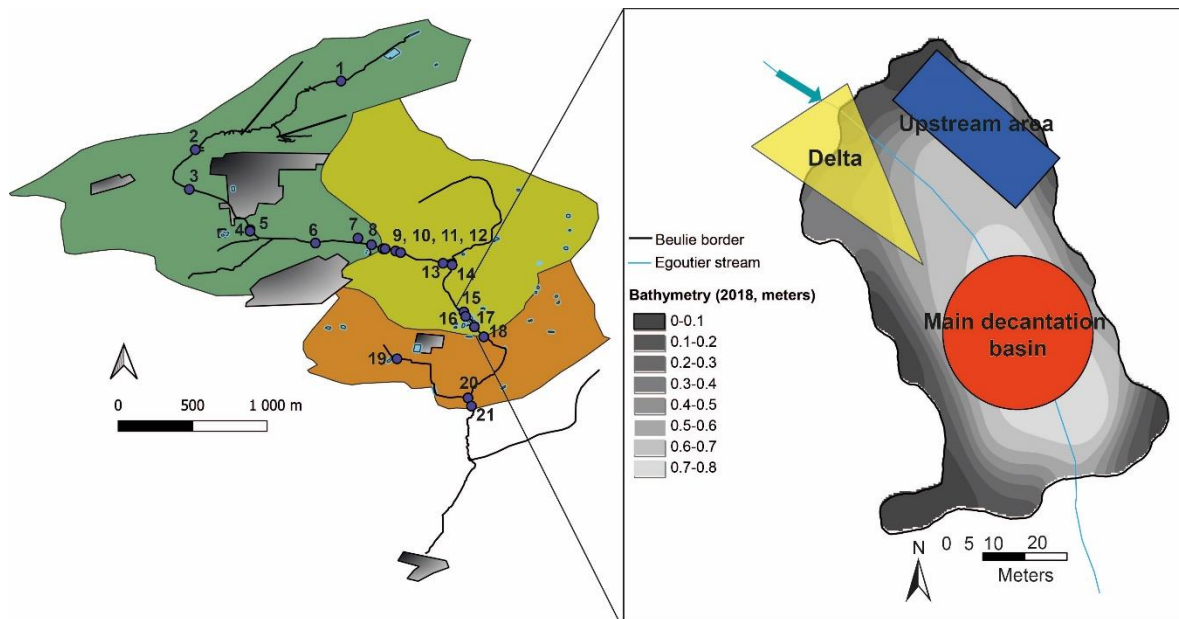


Figure 2. 4: Map representing the sampling stations (45-EG-1 to 21, on the left side) along the Egoutier stream and the investigated areas within the Beulie Pond (on the right side).

4.2. The particulate phase

4.2.1. Suspended particulate matters: the transported particulate phase

SPMs correspond to the erosion products of soils. Since they contribute to biogeochemical cycles and are likely to adsorb contaminants, and notably PPs (Ledieu et al., 2021; Chapter 1), SPMs raised more and more concern (DCE, 2000). They are also sentinels of the effects of land use changes and soil artificialization (Thomas et al., 2004; Murphy, 2020), as well as seasonality variations such as extreme rainfall events (Römken et al., 2001) on erosion processes. In order to follow their transfer and the variations of their characteristics along the Egoutier watershed, GEACOS sediment traps (Simonneau 2020, Figure 2.3) were placed at the three monitored locations also surveying hydrological regimes (i.e. ST1, ST2, ST3, Figure 2.2). These sediment traps comprise riddles of different granulometric cuttings from 1 mm to 0.45 μm , in order to i/ help an *in-situ* sieving and ii/ limit the loss of finer particles.

The transport of SPMs in the Egoutier stream, and their accumulation within the Beulie pond lead to water/sediment interface surface sediments, referred to as the settled particulate phase, which constitutes the particulate phase of interest in the present thesis work.

4.2.2. Beulie pond surface sediments: the settled particulate phase

The Beulie pond represents the rupture in the sedimentary cascade of the Egoutier watershed (Ledieu et al., 2020), causing the settling of SPMs into the delta and then the main basin of the Beulie system. However, in accordance with the bathymetric map (Figure 2.4), particles accumulation might not be homogeneous at the pond scale. Furthermore, the water-column is likely to offer different physico-chemical characteristics than the stream water, resulting for example in variations in OM diagenetic processes (Li et al., 2024). Since surface sediments result from the accumulation of SPMs in the pond, themselves potentially carrying PPs, the particular dynamics of the Beulie pond seem determinant in the fate of PPs and more especially in PPs behaviour in the water-sediment continuum.

Surface sediments were therefore sampled in the three previously described areas: the delta, the upstream area and the main decantation basin. The sampling was performed on a Zodiac boat using an Ekman grab. The collected surface sediments were then conditioned in HDPE bottles, and stored at 4 °C prior to further characterization. Between 2018 and 2023, 43 Ekman grab samples have been collected.

5. Water-sediment continuum: what are their bulk properties and the pharmaceutical product contents of their compartments?

5.1. Aqueous and particulate phase bulk properties

5.1.1. Dissolved organic carbon concentration

The dissolved organic carbon (DOC) was quantified using an elemental TOC-L analyser (Shimadzu). Prior to analysis, water samples were filtered at 0.45 µm, acidified at around pH 2 using concentrated orthophosphoric acid (H₃PO₄) and stored at 4 °C. The day of the analysis, they were diluted by a factor 2 using ultra-pure water (MilliQ grade, 18.2 MΩ). The analytical sequence also included 3 blank ultra-pure water samples (filtered at 0.45 µm on the field, unfiltered also from the field and taken directly from the ultra-pure water distributor). Total nitrogen (TN) was also quantified during the sequence. The calibration was proceeded using a calibration standard (potassium hydrogenophthalate for DOC and potassium nitrate for TN) of known DOC and TN concentrations respectively, and inhouse standards were used as control points.

5.1.2. Surface sediments grain-size distribution

The granulometric distribution is represented here by clay (<2 µm), fine silt (2-20 µm), coarse silt (20-63 µm), fine sand (63-250 µm) and coarse sand (250-1800 µm) contents,

according to the Udden-Wentworth scale, calculated for the 2021 sample set. The granulometric distribution was determined using laser diffraction particle size analyser (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 was emitted with its reflection depending on particles size, which finally allowed to get the particle size as a function of the volume occupied in the cell.

5.1.3. Total organic carbon quantification

Bulk geochemical study of the organic matter was obtained by Rock-Eval pyrolysis to characterize the organic content of natural samples by thermal cracking and to quantify the hydrocarbons (HC) that escape from the studied sample. Analyses were performed using Rock-Eval 6 Turbo (Vinci Technologies). The total organic carbon (TOC, %) content and the Hydrogen Index ($\text{HI} = (\text{S}_2 \cdot 100) / \text{TOC}$ expressed in $\text{mg of HC} \cdot \text{g}^{-1}$ of TOC, with S_2 corresponding to the hydrocarbon generation potential obtained for pyrolysis products from cracking OM, expressed in $\text{mg of HC} \cdot \text{g}^{-1}$ of dried sample, 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 origin of OM 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 is linked with 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).

Prior to analysis, samples were freeze-dried and finely crushed in an agate mortar in order to reach a grain size under $160 \mu\text{m}$. Between 40 and 60 mg of samples were weighted using a precision balance. The standard IFP160000 was used for the calibration.

5.2. Pharmaceutical product contents in the water-sediment continuum

In order to determine the fate of PPs in the water-sediment continuum of the Beulie pond, PPs were quantified in both particulate and aqueous phases, that are respectively surface sediments and water collected at the water-sediment interface.

The analysis was performed using a liquid-chromatography coupled with tandem mass-spectrometers (LC-MS/MS). PPs quantification using this method was relevant, since the limits of quantification for various PPs are generally around 1 ng/g and 1 ng/L .

5.2.1. Pharmaceutical products extraction in aqueous matrices: Solid-phase extraction

PPs were extracted from aqueous samples using Solid Phase Extraction (SPE), prior to analysis with a liquid chromatography coupled with tandem mass spectrometers (LC-MS/MS, Agilent). SPE columns were conditioned with 2x5 mL MeOH and 2x5 mL ultra-pure water prior to extraction. Then, ~200 mL of sample was used for the extraction, spiked with 50 ng of isotopically labeled internal standards. PPs were eluted from the column with 2x5 mL MeOH, prior to evaporation under gentle nitrogen flow. After being reduced to ~500 µL, samples were transferred in vials and frozen until analysis.

5.2.2. Pharmaceutical products in particulate matrices: Pressurized liquid extraction

PPs in sediment samples were extracted following the method described by Le Gaudu et al. (2022). 1.0±0.1 g of sample was spiked with isotopically labeled internal standards (LGC Standards), mixed with 0.5 g of Ethylenedinitrilotetraacetic acid (EDTA) and then extracted with MeOH using pressurized liquid extraction (ASE 350, Thermo) at 100 °C and 1000 psi. The extract was recovered with ultra-pure water, and purified through SPE with the same protocol than aqueous samples, with an additional filtration step at 0.22 µm (Nylon filter, VWR). MeOH was used again to recover extracts, before their injection in LC-MS/MS system (Agilent).

5.2.3. LC-MS/MS analysis

Samples were analyzed using 1200 SL HPLC system (Agilent). Recoveries of PPs were calculated, as well as their respective limits of detection (LOD) and quantification (LOQ) in the particulate and aqueous phases. Recoveries were used to correct the quantification data. The 11 quantified PPs are Carbamazepine (CBZ), Oxazepam (OXA), Diazepam (DIA), Paracetamol (PAR), Tramadol (TRA), Atenolol (ATE), Fluoxetine (FLX), Venlafaxine (VFX), Metoprolol (MTP) and Diclofenac (DIC).

6. What are the properties of the key matrices of the water-sediment continuum compartments likely to carry pharmaceutical products?

The natural matrices refer here to the components of the compartments composing the water-sediment continuum (Figure 6). Many matrices are part of both water and sediment composition, and some of them are particularly reactive and have a known affinity for PPs (*cf* Chapter 1). These matrices were therefore finely characterized, in order to identify their properties potentially responsible for PPs adsorption on the particulate phase.

6.1. Organic matter

6.1.1. Organic matter elemental composition

Sediment samples elemental composition was determined using elementary Flash CHNS analyzer. Samples were pre-treated with hydrochloric acid (HCl) and hydrofluoric acid (HF) in order to eliminate carbonate and silicate phases, respectively, then finely crushed in an agate mortar. About 2 mg of powder were introduced in a tin capsule and analyzed in the oxidation/reduction oven, heated at a temperature reaching between 900 and 1000°C. The oxidation of tin raised the temperature to 1800°C, ensuring the transformation of all organic compounds into gases, including CO₂, NO₂, H₂O and SO₂. These gases are then separated thanks to a gas chromatography column, before being detected using a thermal detector. The amount of oxygen was determined by subtraction ($\%O = 100 - (\%C + \%H + \%N + \%S)$). The percentage of C, H, N, S, O were converted in % mol using the molar weight of each element (i.e. 12.01 g/mol, 1.01 g/mol, 14.01 g/mol, 32.07 g/mol and 15.99 g/mol, respectively).

6.1.2. Organic matter typology: Quantitative palynofacies analysis

Quantitative palynofacies analysis (QOP) consists in the optical identification and quantification of the organic constituents present in a constant volume of sediment (1 cm³) or in one gram of soil, after elimination of carbonate and silicate phases by hydrochloric and hydrofluoric acid 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).

6.1.3. Organic matter composition: organic matter families and functional groups

The Rock-Eval S2 signals were deconvoluted in order to identify the different fractions of organic matter according to their respective peak temperatures (Hetényi et al., 2005; Sebag et al., 2006; Simonneau et al., 2013). As the number of organic matter fractions is hardly predictable, the consensus adopted in most of studies proposes a deconvolution of the signal into 4 fractions (F1 to F4), corresponding to 4 main clusters (300-320 °C; 360-380 °C; 430-450 °C; > 470 °C), as showed by previous works (Di Giovanni et al., 1998; Noël et al., 2001; Disnar et al., 2003; Sebag et al., 2006). The 300-320 °C cluster is attributed to labile bio macromolecules part of plants and soil litter composition. The 360-380 °C cluster is attributed to resistant biopolymers like lignin and cellulose. The 430-450 °C cluster is attributed to humic substances and the > 470 °C cluster to mature geo-macromolecules. The deconvolution was performed using Origin lab PRO, and by fixing 4 temperatures: 305.6 ± 5.4 °C, 370.2 ± 5.0 °C, 438.4 ± 8.6

°C and 483.1 ± 9.6 °C, calculated after Disnar et al. (2003), as mean values of peak temperatures of the four fractions obtained after the deconvolution of the S2 signals of podzols and spodic cambisol (n=12).

The identification of OM functional groups in the 5 grain-size fractions was determined using Fourier-Transformed InfraRed (FTIR) Spectrophotometry. To proceed so, about 300 mg of KBr salt were mixed with about 1 mg of dried sample (after the removal of carbonate and silicate phases). The mixture was finely crushed in an agate mortar, then the powder was pressed at 8 tons during 10 minutes using a hydraulic press. The resulting pellets were stored safe from humidity to limit the characteristic absorbance peak of water on FTIR spectra (Artz et al., 2008; $\sim 3400\text{ cm}^{-1}$).

Pellets were analyzed by mid-infrared microSpectrophotometry, using a Continuum microscope coupled to a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, USA) with an internal source (Globar). The equipment of the microscope includes a liquid-nitrogen cooled $50\text{ }\mu\text{m}$ MCT detector, a 32x infinity-corrected Schwarzschild type objective (NA = 0.65, WD = 7 mm) and a 32x condenser featured in the confocal mode. The confocal geometry was allowed by the use of the 'single aperture dual path mode'. The projected pixel size was $50 \times 50\text{ }\mu\text{m}$. Each FTIR spectrum was recorded in the $4000\text{--}650\text{ cm}^{-1}$ spectral range, with a resolution of 8 cm^{-1} and 128 scans. The KBr pellet spectrum was recorded several times during the analysis, in order to consider atmospheric CO_2 , CH_4 and moisture variations, and was used as background for sample pellet spectra recordings. FTIR spectra were postprocessed using OPUS 7.5 (Bruker), with baseline correction (Mozhdehei et al., 2024).

6.2. Mineralogical phases: XRD measurements

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 parafofocussing 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 minutes 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. The OM removal procedure involved bulk sample freeze-drying, digestion with 6 % hydrogen peroxide, repeated rinsing with ultrapure water followed by centrifugation, overnight drying at 45 °C, and crushing 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).

7. Pharmaceutical products onto surface sediments: what are the factors susceptible to influence the stability of the trapping?

7.1. Physico-chemical conditions in the water-column

Physico-chemical vertical profiles were performed in September 2023 and 2024 at three locations within the Beulie pond: the “Delta”, the “Upstream area” and the “Main decantation basin”. The measured parameters were the pH, the electrical conductivity, the redox potential, the dissolved O₂ and the temperature. The pH probe was calibrated using buffer solutions of pH 4.010; 7.000 and 10.011 provided by WTW. The electrical conductivity probe was calibrated using a KCl solution corresponding to 1413 $\mu\text{S}/\text{cm}$ at 25 °C, also provided by WTW. The measurements were proceeded from the water surface to the sediment-water interface, each 5 cm, and the data were continuously registered during 1 min at each step with a 1 second interval.

7.2. Organic matter early diagenesis: grain-size fractionation

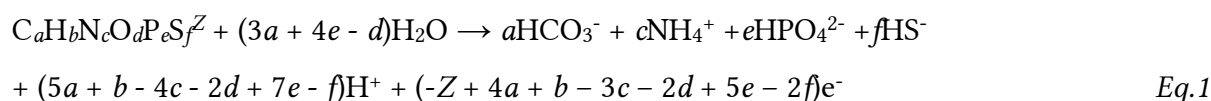
Complementarily to the determination of the surface sediment granulometric distributions, surface sediments were fractioned into 5 granulometric classes using wet-sieving, in order to proceed a further geochemical and mineralogical characterization of each class. The chosen granulometric classes were: ≥ 1 mm, 250 μm – 1 mm, 160 μm – 250 μm , 63 μm – 160 μm and ≤ 63 μm . The wet sieving method was chosen in order to get a granulometric distribution as representative as possible of the natural environment, without breaking bigger

particles in smaller ones. Sediments previously stored at 4 °C were sieved using either pond water collected at the water/sediment interface, in order to keep as much as possible the sediment in physico-chemical conditions close to the ones occurring in the field, or ultra-pure water, in order to sieve the sediment without adding dissolved species. Both pond water and ultra-pure water were sprayed thanks to a painting gun connected to a compressed air pipe. The $\leq 63 \mu\text{m}$ class was recovered by centrifugation at 10,000 g during 15 minutes. The supernatant, named hereafter the sieving-water, was filtered at $0.45 \mu\text{m}$ and stored at 4 °C until analysis. The pellet corresponding to the $\leq 63 \mu\text{m}$ class was freeze-dried and stored until analysis, as well as the $\geq 1 \text{ mm}$, $250 \mu\text{m} - 1 \text{ mm}$, $160 \mu\text{m} - 250 \mu\text{m}$ and $63 \mu\text{m} - 160 \mu\text{m}$ classes recovered from the riddles.

7.3. Organic matter reactive properties

In the environment, OM and organic compounds in general are subjected to diagenetic processes, resulting in either their degradation or preservation. From the thermodynamic point of view, the fate of organic compounds in a natural system will rely on the ability of the natural system components to preserve or degrade them, which can be interpreted as an amount of needed energy (Boye et al., 2017).

The Gibbs free energy represents here the amount of energy needed to oxidize the OM in the standard state. La Rowe and Van Cappellen (2011) evidenced a linear relationship between the Gibbs free energy and the nominal oxidation state of carbon (NOSC), calculated on the basis of the elemental composition of a variety of organic matter and organic compounds. This relationship therefore allows to calculate the Gibbs free energy with the knowledge of the OM NOSC value. The relation below gives the oxidation half reaction that determines the average oxidation state of carbon:



where the subscripts a, b, c, d, e and f correspond to the stoichiometric coefficients of the elements C, H, N, O, P and S respectively and Z corresponds to the net charge of the organic compound. The nominal oxidation state of carbon corresponds to the ratio between the number of electrons exchanged and the number of carbon atoms. As the carbon in the half

reaction is considered fully oxidized, meaning in the (+4) oxidation state, the NOSC is calculated as:

$$\text{NOSC} = -((-Z + 4a + b - 3c - 2d + 5e - 2f)/a) + 4 \quad \text{Eq.2}$$

The NOSC can be “easily” determined from the chemical formula of known organic compounds, but in the case of natural samples, the elemental composition is needed.

La Rowe and Van Cappellen (2011) empirically determined the linear relationship between the free Gibbs energies and the NOSC, using organic compound with known thermodynamic properties, which gives

$$\Delta G_r^0 = 60.3 - 28.5 \cdot \text{NOSC} \quad \text{Eq.3}$$

At the standard state:

$$K = Q \quad \text{Eq.4}$$

with K the equilibrium constant of the half oxidation reaction, and Q the reaction quotient, which results in:

$$\Delta G_r^0 = -2.3 \cdot RT \log(Q) \quad \text{Eq.5}$$

where R designates the gas constant, equal to 8.314 J.mol⁻¹ and T the temperature in K. This relation allows to calculate Q, which also corresponds to:

$$Q = \prod (ac_i)^{\nu_i} \quad \text{Eq.6}$$

where ac_i is the activity of the specie i part of the half oxidation reaction, and ν_i corresponds to the stoichiometric coefficient of the specie i. ν_i is positive for the products and negative for the reactants. This leads to:

$$\begin{aligned} \log(K) = & \log(ac(\text{HCO}_3^-)) + c \cdot \log(ac(\text{NH}_4^+)) + e \cdot \log(ac(\text{HPO}_4^{2-})) + f \log(ac(\text{HS}^-)) - \\ & (5a + b - 4c - 2d + 7e - f) \cdot \text{pH} - (-Z + 4a + b - 3c - 2d + 5e - 2f) \cdot \text{pe} \\ & - \log(ac(\text{C}_a\text{H}_b\text{N}_c\text{O}_d\text{P}_e\text{S}_f\text{Z})) \end{aligned} \quad \text{Eq.7}$$

with the stoichiometric coefficient of the different species of the half oxidation reaction normalized to 1mol of C. The pe can also be written as:

$$\text{pe} = \frac{F \cdot Eh}{2.33 \cdot RT} \quad \text{Eq.8}$$

with E_h the redox potential, F (96,485 C) the Faraday constant, R ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$) the gas constant and T (298.15 K) the temperature. The activity of the organic compound can therefore be calculated with Eq.7 as a function of E_h , since the pH is given and since the activities of the other dissolved species can be estimated. It means however that the activity of the organic compound is available in a specific environment, of known pH range and water ionic composition. The relative activity of the organic compound can also be calculated as the ratio between its activity and the sum of the activities of the other organic compounds present in the natural system.

8. What are the kinetics and mechanisms involved in the adsorption/desorption of pharmaceutical products onto/from sediments?

8.1. Stability of the adsorption: kinetic experiment

In order to evaluate the stability of PPs adsorption on the particulate phase, and the kinetics of these mechanisms for given physico-chemical conditions, an adsorption/desorption kinetic experiment was performed.

This experiment consisted in putting into interaction water collected at the water/sediment interface of the Beulie pond, the same that was used for the wet-sieving procedure (*Section 7.2*) with surface sediment. To proceed so, about 300 g of wet surface sediment were put into a 4 L HDPE bottle, and 3.5 L of pond water were added. The bottle was agitated during 10 minutes, after what 0.15 mL of the aqueous phase were sampled, centrifuged at 10,000 g during 5 minutes, filtered at $0.45 \mu\text{m}$ and saved for later PPs quantification using LC-MS/MS analysis. In order to conserve to same solid/liquid ratio, the bottle was completed with 0.15 mL of pond water and agitated until 30 minutes (time counted from the beginning of the experiment). The same sequence was repeated, and the bottle agitated until 60 minutes (time counted from the beginning of the experiment) (Figure 2.5). At each sampling, the redox potential, the dissolved O_2 , the electrical conductivity and the pH were measured.

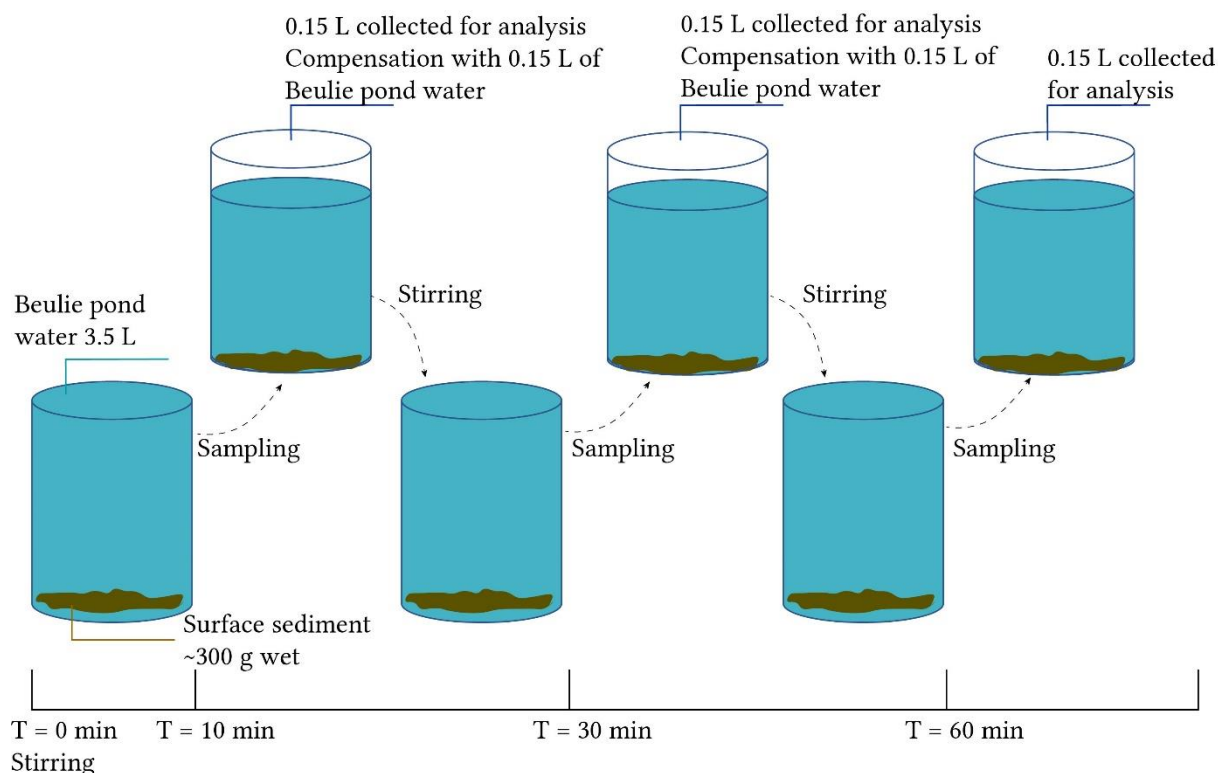


Figure 2. 5: Adsorption/desorption experiment performed to determine PPs exchange dynamics between Beulie pond water and surface sediment.

8.2. Bonding mechanisms: batch adsorption experiments

8.2.1. Batch sample preparation

Batch adsorption experiments were constructed in order to put a solid phase in interaction with a solution enriched in PPs. For this experiment, the adsorbed concentration in PPs onto Beulie pond surface sediments was compared with the one onto a referenced Kaolinite, KGa-2, provided by the Clay Mineral Society. The 2 selected PPs were Tramadol (TRA) and Carbamazepine (CBZ), both provided by Sigma Aldrich.

Batch samples were performed in 50 mL PTFE tubes (Fisher Scientific). The particulate phase mass was fixed at 200 mg and the aqueous phase volume was fixed at 40 mL. Three different batch samples were prepared in triplicate. The first one tested the adsorption of CBZ and TRA onto Beulie pond surface sediment, and contained 200 mg of dried and finely crushed surface sediment. The second one, tested the adsorption of CBZ and TRA onto Kaolinite KGa-2, and comprised 200 mg of Kaolinite KGa-2 (Clay Mineral Society). The last one, evaluating the influence of an addition of kaolinite on the adsorption of CBZ and TRA onto surface sediment was prepared with 150mg of surface sediment and 50mg of Kaolinite KGa-2. The

same CBZ or TRA solutions were used for the aqueous phase of all batch samples. The latter were prepared in a CaCl_2 0.01 M solution, whose ionic composition was close to the one of the Beulie pond water without dissolved organic carbon interferences.

Blank samples, with the same particulate phase than the batch samples, but with an aqueous phase comprising only the CaCl_2 solution, were also prepared in triplicate (Figure 2.6). All the samples were then stirred during 24 h in a rotative stirrer.

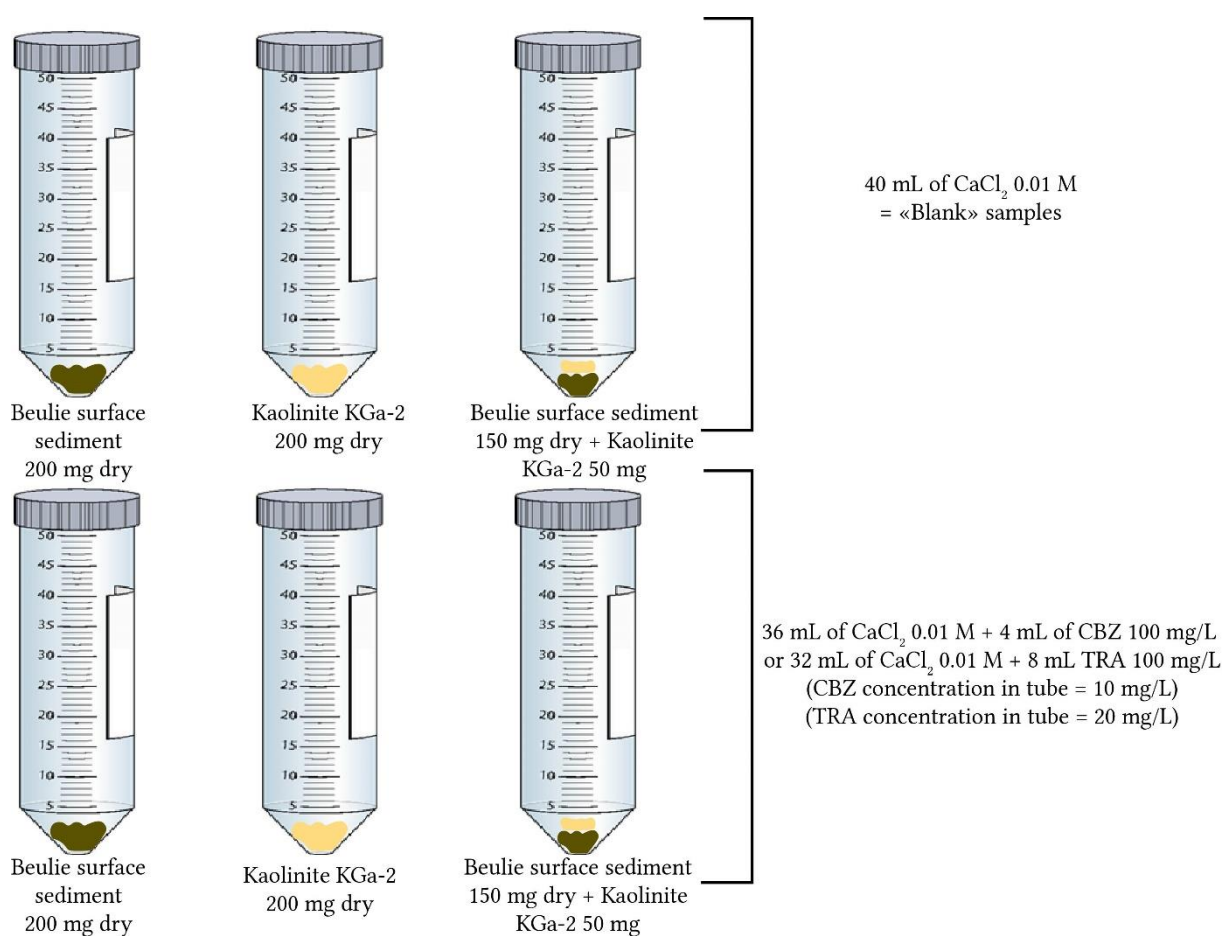


Figure 2. 6: Preparation of batch adsorption experiments using to PPs (CBZ and TRA) and 3 different particulate phases: Beulie pond surface sediments, Kaolinite KGa-2 and a mix containing 75 wt% of Beulie pond sediments and 25 wt% of Kaolinite KGa-2.

8.2.2. Determination of pharmaceutical products initial concentrations in batches

The quantification of PPs in the dissolved phase of batch samples was performed using UV-Visible Spectrophotometry, which consists in measuring their absorbance as a function of the wavelength, the latter ranging from 200 to 750 nm. Quartz vials were used for the

measurement. They were previously cleaned using Dichloromethane (DCM) followed by a 1 M hydrochloric acid cleaning and were then rinsed 10 times using ultra-pure water.

In order to determine the chromophores of CBZ and TRA, corresponding to their main absorbance peak, a preliminary calibration of CBZ and TRA solutions of different concentrations, in the 0.25 - 10 mg/L range, was performed (Figure 2.7).

According to the CBZ and TRA absorbance specters, the wavelengths of their chromophores were 285 ± 2 nm and 271 ± 2 nm, respectively. Indeed, if chromophores with higher amplitudes appeared in the 210 - 220 nm range for both PPs, it was estimated based on previous tests that at these lower wavelengths, a matrix effect due to the desorption of sediment components during the stirring might occur. The concentrations of the solutions in CBZ and TRA used for the batch adsorption experiments were therefore fixed at 10 mg/L and 20 mg/L, respectively. Indeed, at 10 mg/L, the chromophore of CBZ was well defined, while the one of TRA had a corresponding absorbance value under 0.1. To manage the adsorption of TRA onto the solid phase, which would decrease the TRA concentration in the dissolved phase, and result in a weaker absorbance amplitude, the initial concentration of TRA in batches was increased to 20 mg/L.

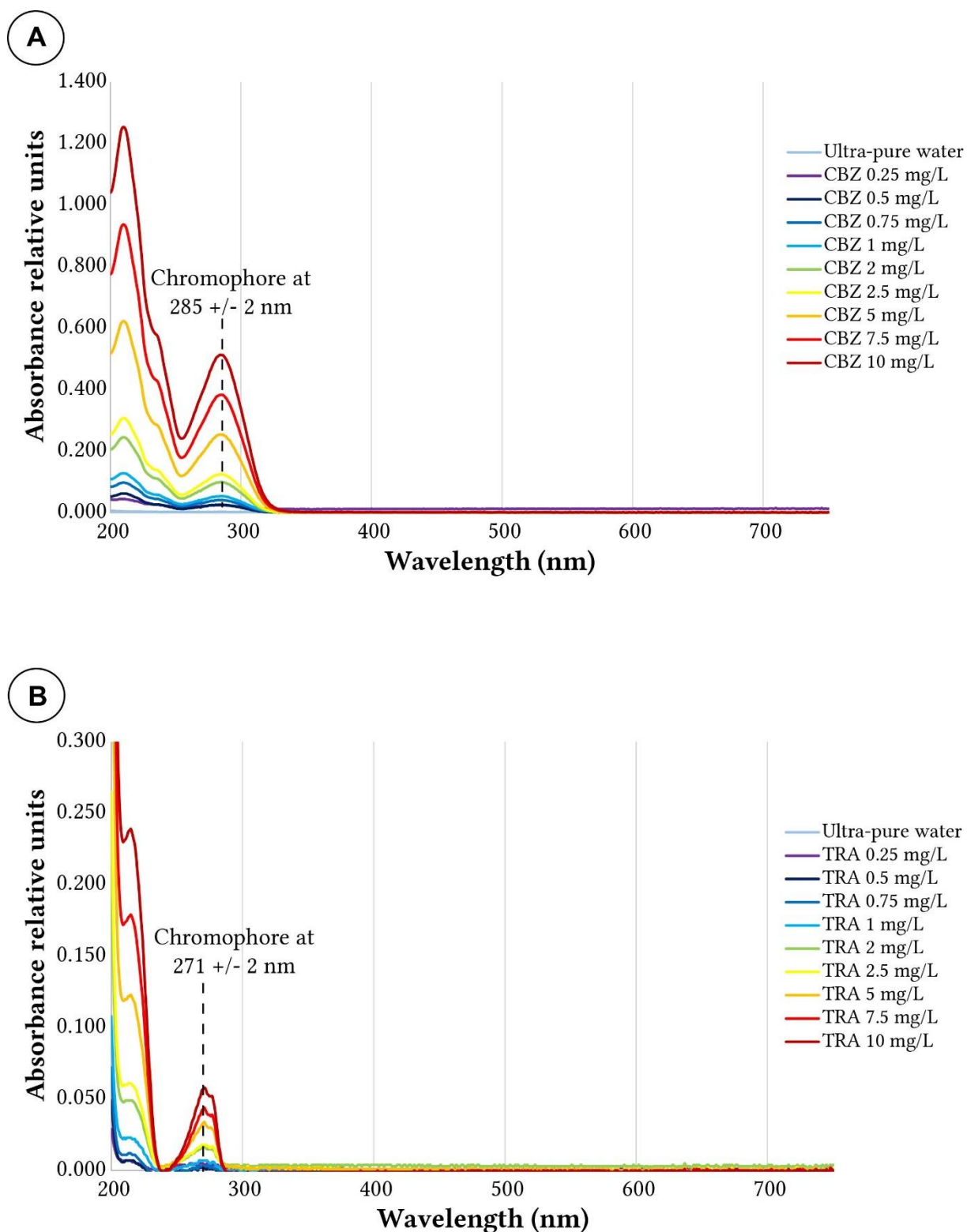


Figure 2. 7: Calibration of carbamazepine (A) and tramadol (B) UV-Visible absorbance at different concentrations in the 0.25 - 10 mg/L range, in order to identify the wavelength of their chromophores, that will be used for the quantification of their concentrations in batch solutions.

8.2.3. Pharmaceutical products quantification in the aqueous phase of batch samples: UV-Visible Spectrophotometry

At equilibrium, batch samples were centrifuged 5 min at 10,000 g. The supernatant was filtered at 0.45 μm , and the pellet was stored in a freezer waiting for later freeze-drying. The quantification of CBZ and TRA concentrations in the dissolved phase was performed using the method of measured addition (Figure 2.8), corresponding to an addition of a known increasing volume of a 100 mg/L CBZ or TRA solution prepared in CaCl_2 0.01 M. The measured absorbance plotted as a function of the added concentration of each measured addition results in a linear regression, and the batch sample concentration corresponds to the offset, that is to say the concentration for which Absorbance is equal to 0. The detailed calculation is presented in Appendix 6.

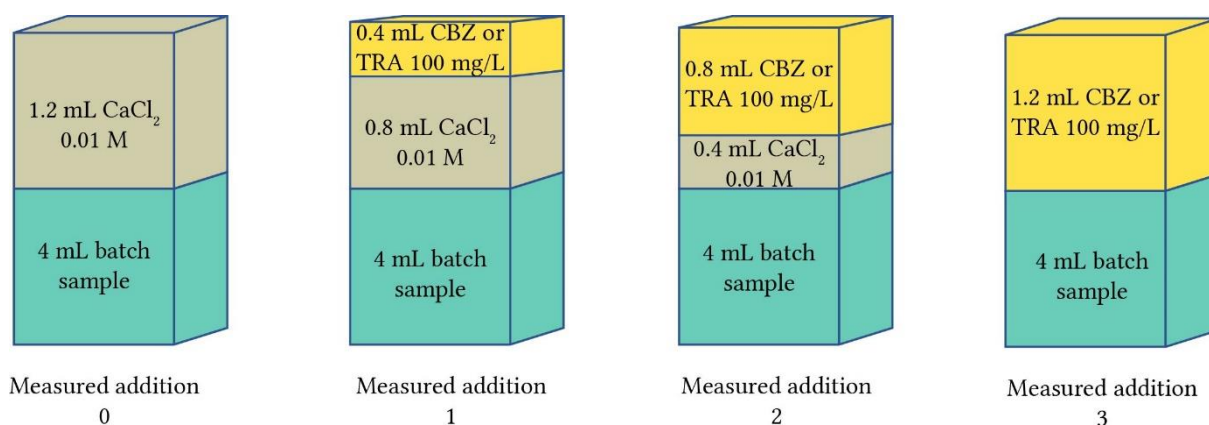


Figure 2. 8: Illustration of the quantification of PPs using the measured addition method.

8.2.4. Characterization of batch sample particulate phases after the experiment

The pellets recovered after the centrifugation of batch samples were freeze-dried and finely crushed prior to FTIR analysis, the latter allowing to identify the particulate phase functional groups before and after its interaction with PPs.

Prior to FTIR analysis, samples were dried overnight in the oven at 110 $^{\circ}\text{C}$, as well as KBr salt, used as background, because transparent for in infrared Spectrophotometry. Between 0.5 and 1 mg of samples were then weighted using a high precision scale. They were then mixed with between around 380 mg of KBr salt, and finely crushed. The mixture was then flattened at 8 tones during 10 minutes to form a pellet. Pellets were then analyzed using the Vertex 70v from Bruker. The wavelength was ranging from 500 cm^{-1} to 4000 cm^{-1} and 128 scans were

proceeded for each sample. The KBr pellet was used as background for each measurement. After analysis, absorbance specters were processed using the OPUS interface.

In order to determine the functional groups of CBZ and TRA, likely to create bonds with those of the different solid phases, two aliquots of pure molecules were preliminarily analyzed (Figure 2.9).

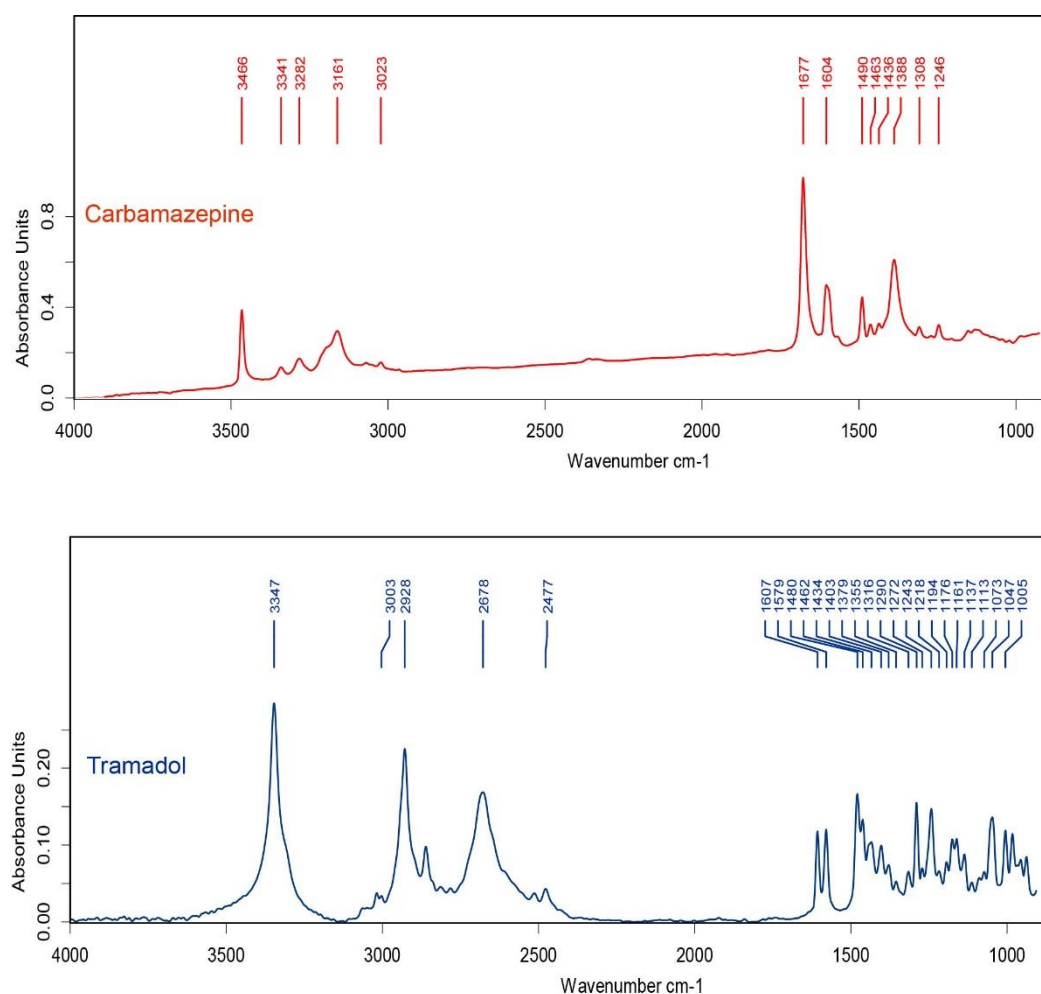


Figure 2. 9: Fourier Transform Infrared specters of Carbamazepine and Tramadol.

9. Summary of surface sediment and water samples collected at the water/sediment interface of the Beulie pond between September 2018 and September 2024

Surface sediment and water samples have been collected between September 2018 and September 2024 at the water/sediment interface of the Beulie pond. The following tables

(Table 2.1 and Table 2.2) present, for each sampling set, the number of samples, the context of sampling and the analysis and measurements performed on aqueous and particulate phases, as well as the contributors and the collaborations involved.

Table 2. 1: Summary of sampling, analysis and measurements performed on surface sediments collected at the water/sediment interface of the Beulie pond between September 2018 and September 2024.

Year of sampling (September -)	Field team	Number of samples	Context of sampling	Analysis/Measurements (Lab, Analytical Platform, people involved)
2018	Lauriane Ledieu, Anaëlle Simonneau, Marielle Hatton	4	Thesis of Lauriane Ledieu	Total Organic Carbon quantification and Organic Matter characterization: Rock-Eval pyrolysis (ISTO Lab, GEOMIN Platform, Lauriane Ledieu, Anaëlle Simonneau, Claude Le Milbeau, Rachel Boscardin)
2020	Anaëlle Simonneau, Marielle Hatton, Master 2 Geo2Env students	10	OBSCURE Observatory monitoring	Total Organic Carbon quantification and Organic Matter characterization: Rock-Eval pyrolysis (ISTO Lab, GEOMIN Platform, Lauriane Ledieu, Anaëlle Simonneau, Claude Le Milbeau, Rachel Boscardin, Master 2 Geo2Env students)
2021	Anaëlle Simonneau, Marielle Hatton, Master 2 Geo2Env students	15	Master 2 Internship of Gauthier Bernier-Turpin	- Total Organic Carbon quantification and Organic Matter characterization: Rock-Eval (ISTO Lab, GEOMIN Platform, Gauthier Bernier-Turpin, Anaëlle Simonneau, Claude Le Milbeau, Rachel Boscardin) - Sediment samples grain-size distribution; Laser-granulometry measurements (ISTEP Lab, Gauthier Bernier-Turpin, Laurence Le Callonnec) - Pharmaceutical Products quantification: LC-MS/MS (METIS Lab, Thomas Thiebault, Fabrice Alliot)
2022	Anaëlle Simonneau, Marielle Hatton, Master 2 Geo2Env students	11	OBSCURE Observatory monitoring	Total Organic Carbon quantification and Organic Matter characterization: Rock-Eval pyrolysis (ISTO Lab, GEOMIN, Anaëlle Simonneau, Claude Le Milbeau, Rachel Boscardin, Master 2 Geo2Env students)
2023	Amélie Humbrecht, Anaëlle Simonneau, Marielle Hatton, Nicolas Freslon, Master 2 Geo2Env students	3	Thesis of Amélie Humbrecht	- Total Organic Carbon quantification and Organic Matter characterization: Rock-Eval (ISTO Lab, GEOMIN Platform, Amélie Humbrecht, Claude Le Milbeau) - Pharmaceutical Products quantification: LC-MS/MS (METIS Lab, Amélie Humbrecht, Thomas Thiebault, Fabrice Alliot) - Organic particles characterization: Quantitative Organic Petrography (ISTO Lab, GEOMIN Platform, Anaëlle Simonneau, Marielle Hatton) - Crystalline phases characterization and quantification: X Ray Diffraction measurements (CATRIN Institute, NanoEnviCz Research Infrastructure, Olomouc, Czech Republic, Amélie Humbrecht, Veronika Veselská, Josef Kašlik)

2024	Amélie Humbrecht, Anaëlle Simonneau, Marielle Hatton, Nicolas Freslon, Master 2 SSP-DE students	3	Thesis of Amélie Humbrecht	• Total Organic Carbon quantification and Organic Matter characterization: Rock-Eval (ISTO Lab, GEOMIN Platform, Amélie Humbrecht, Claude Le Milbeau) • Pharmaceutical Products quantification: LC-MS/MS (METIS Lab, Amélie Humbrecht, Thomas Thiebault, Fabrice Alliot) • Fourier-Transformed Infrared Spectroscopy (ISTO Lab, Experimentation Platform, Amélie Humbrecht, Aneta Slodczyk)
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Table 2. 2: Summary of sampling, analysis and measurements performed on water samples collected at the water/sediment interface of the Beulie pond between September 2023 and September 2024.

Year of sampling (September -)	Field team	Number of samples	Context of sampling	Analysis/Measurements (Lab, Analytical Platform, people involved)
2023	Amélie Humbrecht, Anaëlle Simonneau, Marielle Hatton, Nicolas Freslon, Master 2 Geo2Env students	3	Thesis of Amélie Humbrecht	• Physico-chemical profiles in the Beulie pond (Field team) • Pharmaceutical Products quantification: LC-MS/MS (METIS Lab, Amélie Humbrecht, Thomas Thiebault, Fabrice Alliot) • Dissolved Organic Carbon quantification: TOC-L Analyzer (ISTO Lab, GEOMIN Platform, Nicolas Freslon, Amélie Humbrecht)
2024	Amélie Humbrecht, Anaëlle Simonneau, Marielle Hatton, Nicolas Freslon, Master 2 SSP-DE	3	Thesis of Amélie Humbrecht	• Physico-chemical profiles in the Beulie pond (Field team) • Pharmaceutical Products quantification: LC-MS/MS (METIS Lab, Amélie Humbrecht, Thomas Thiebault, Fabrice Alliot) • Dissolved Organic Carbon quantification: TOC-L Analyzer (ISTO Lab, GEOMIN Platform, Nicolas Freslon, Amélie Humbrecht) • Major elements quantification: Ionic chromatography (ISTO Lab, GEOMIN Platform, Nicolas Freslon, Amélie Humbrecht)

Chapter 3. Sediments accumulation in retention areas: influence of receptacle morphology and particulate phase characteristics



The present Chapter investigates the spatial distribution of the reactive matrices of the particulate phase, in particular organic matter and clay minerals, at the Beulie pond scale, and questions moreover the effect of sediment composition and accumulation on pharmaceutical product content spatial distributions. To answer this question, a high-resolution sampling of the water/sediment interface sediment was performed between 2018 and 2023, resulting in the collection of 43 surface sediment samples.

The quantification of total organic carbon content and complementary Rock-Eval parameters, the determination of the grain-size distribution of surface sediments and the quantification of pharmaceutical products in surface sediments sampling set collected in 2021 were part of the Master Internship of Gauthier Bernier-Turpin.

The quantification of organic palynofacies was performed in the context of the Master Internship of Arthur Jouannetaud on the sampling set collected in 2023.

This study is presented in the form of a research paper, published in Applied Geochemistry in June 2025: Humbrecht, A., Simonneau, A., Thiebault, T., Bernier-Turpin, G., Le Milbeau, C., Veselská, V., ... & Le Forestier, L. (2025). *Effect of sediment composition and accumulation on pharmaceutical product spatial distributions at the suburban pond scale (Beulie pond, SNO Observil, France)*. *Applied Geochemistry*, 190(10648), 7. <https://doi.org/10.1016/j.apgeochem.2025.106487>.

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The edited version is available in Appendix 1 and the supplementary materials are available in Appendix 2.

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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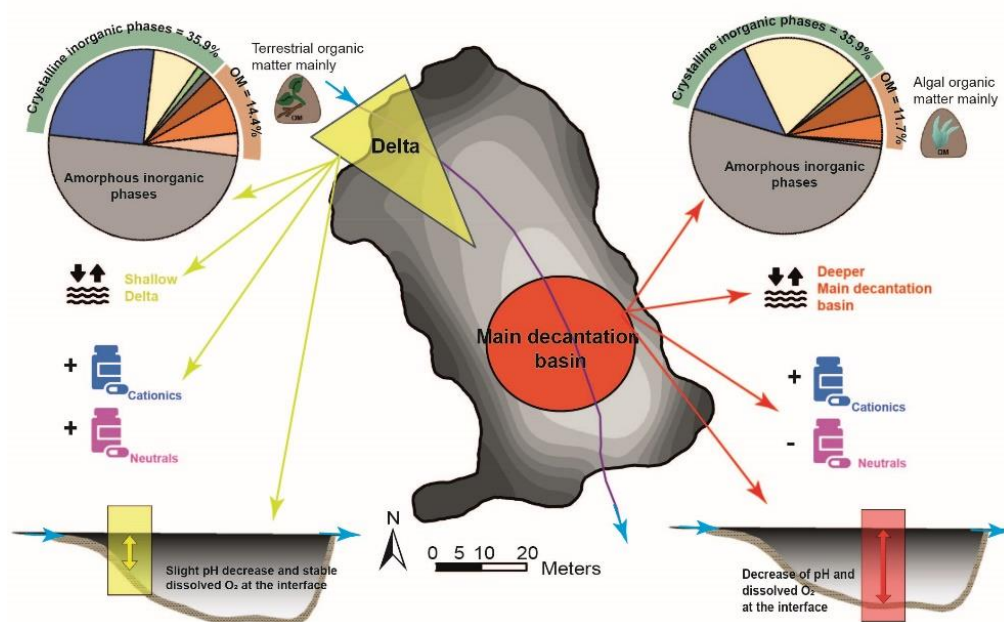
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Keywords: Pond sediment, Organic matter, Kaolinite, Pharmaceutical Products, Spatial distribution

Highlights:

- Surface sediment samples from suburban pond exhibit a spatial heterogeneity
- Extensive sediment characterization clarifies pharmaceutical products distribution
- Spatial patterns reflect sedimentation dynamics and hotspot location in the basin

Graphical abstract



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 ($14.5 \pm 2.2\%$), and particularly terrigenous organic matter and neutral PPs, while the main decantation area mostly fine particles ($58.2 \pm 7.7\%$), 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 (Romanic et al., 2023, Castano-Ortiz et al., 2024), and suspended particulate matters (SPMs, 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 represent one of the most important sources of anthropogenic contaminants (Jacob et al., 2020; Ledieu et al., 2021; Thiebault et al., 2021).

The behaviour 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 SPMs 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. SPMs), can act

as a carrier phase for contaminants via sorption reactions (Al-Khazrajy and Boxall, 2016), including for hydrophilic substances such as PPs.

SPMs 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 centre 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 m². The catchment area drained by the pond covers a surface area of 6.3 km² 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 (Figure 3.1). 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.

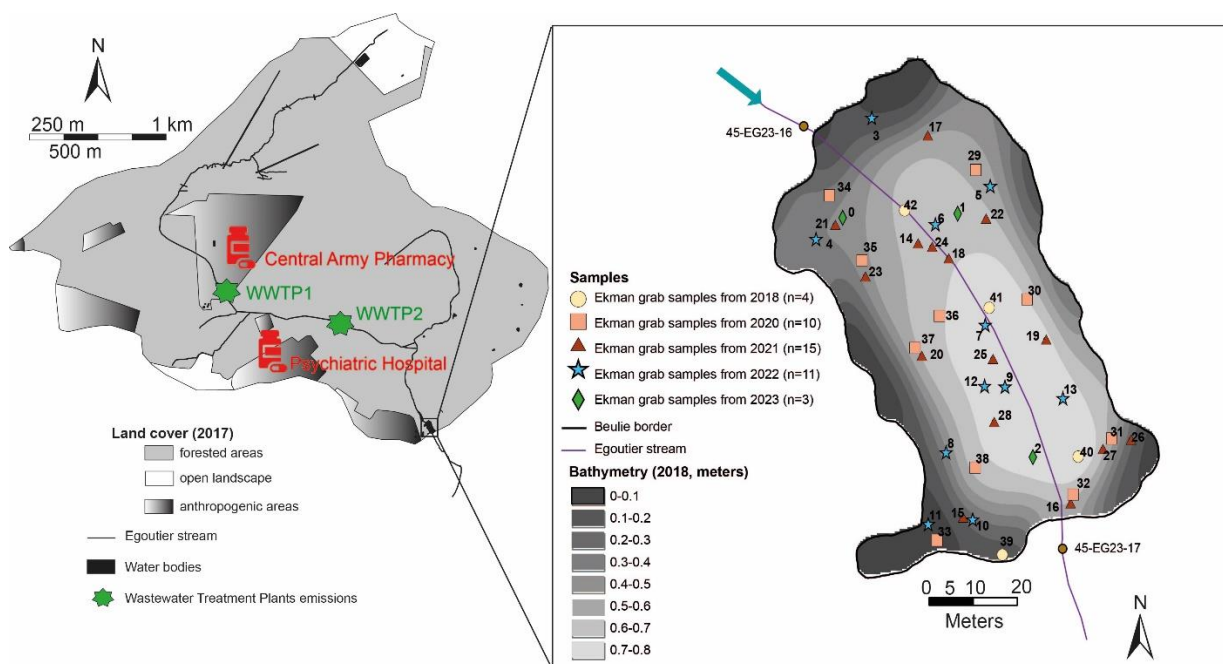


Figure 3. 1: Map representing the Beulie pond catchment area with information about soil occupation collected from Corine Land Cover data from 2017. The Egoutier stream is represented by the black continuous line. The two wastewater treatment plants connected to 1- the central army pharmacy and 2- a 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 to 42) for purposes of simplification.

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 ($<63\ \mu\text{m}$). 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 organic matter, 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 thermal cracking and to quantify the amount of hydrocarbons (HC) that escape from the studied sample. Analyses were performed using Rock- Eval 6 Turbo (Vinci Technologies). The TOC (%) and the Hydrogen Index ($\text{HI} =$

(S2*100)/TOC expressed in mgHC.g⁻¹TOC, 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 cm³) 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 µm), fine silt (2–20 µm), coarse silt (20–63 µm), fine sand (63–250 µm) and coarse sand (250–1800 µm) contents, according to the Udden- Wentworth scale, calculated for 2021 sample set. The granulometric distribution was determined using laser diffraction particle size analyser (Beckman Coulter, LS 13 320 XR). The fine particles fraction (FP, i.e. particle size ≤63 µm), 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 Co Kα 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 reanalysed 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 2 θ 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 analysed 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 3.1. 1.0 $\pm$ 0.1 g of sample was spiked with isotopically labelled internal standards, and 50 ng of each were added (LGC Standards), mixed with 1 g of EDTA and then extracted with 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 $\times$ 150 mg $\times$ 30 μ m, Macherey-Nagel). PP were eluted using 2x5mL of MeOH, and then dried under nitrogen flow, and filtered at 0.22 μ m (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.

Table 3. 1: PPs dissociation constants (P_{ka}), dominant forms at pH between 7 and 8 and octanol-water partition coefficients ($\log K_{ow}$). ^aAmirdehi et al. (2017), ^bCisneros-Covarrubias et al. (2022), ^cLi et al. (2019), ^dCorreia-Sa et al. (2021), ^ewww.drugbank.ca and Knox et al. (2024), ^fThiebault et al. (2021), ^gThiebault et al. (2017), ^hBendz et al. (2005), ⁱLam et al. (2004), ^jZhang et al. (2020), ^kLöffler et al. (2005).

	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 ^c	Neutral	High ^k	3.34 ^f
Diazepam	2.9 ^e	Neutral	Moderate ^k	2.70 ^f
Paracetamol	9.5 ^e	Neutral	Low ⁱ	0.46 ^f

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 (Figure 3.2 A). The mean TOC content at the pond scale is equal to 12.7 ± 2.0 % (Table S2.1). 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 (Figure 3.2 B). QOP showed 2 different trends in palynofacies distribution within the 3 sediment samples analysed. More than 50 % of sample 45-BE23-BE1 (#0 on Figure 3.2 C), located in the pond's delta, is rich in ligno- cellulosic fragments, coming from upper vegetation debris and terrestrial origin. Samples 45-BE23-BE2 (#1 on Figure 3.2 C) and 45-BE23-BE3 (#2 on Figure 3.2 C), 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 (Figure 3.2 C).

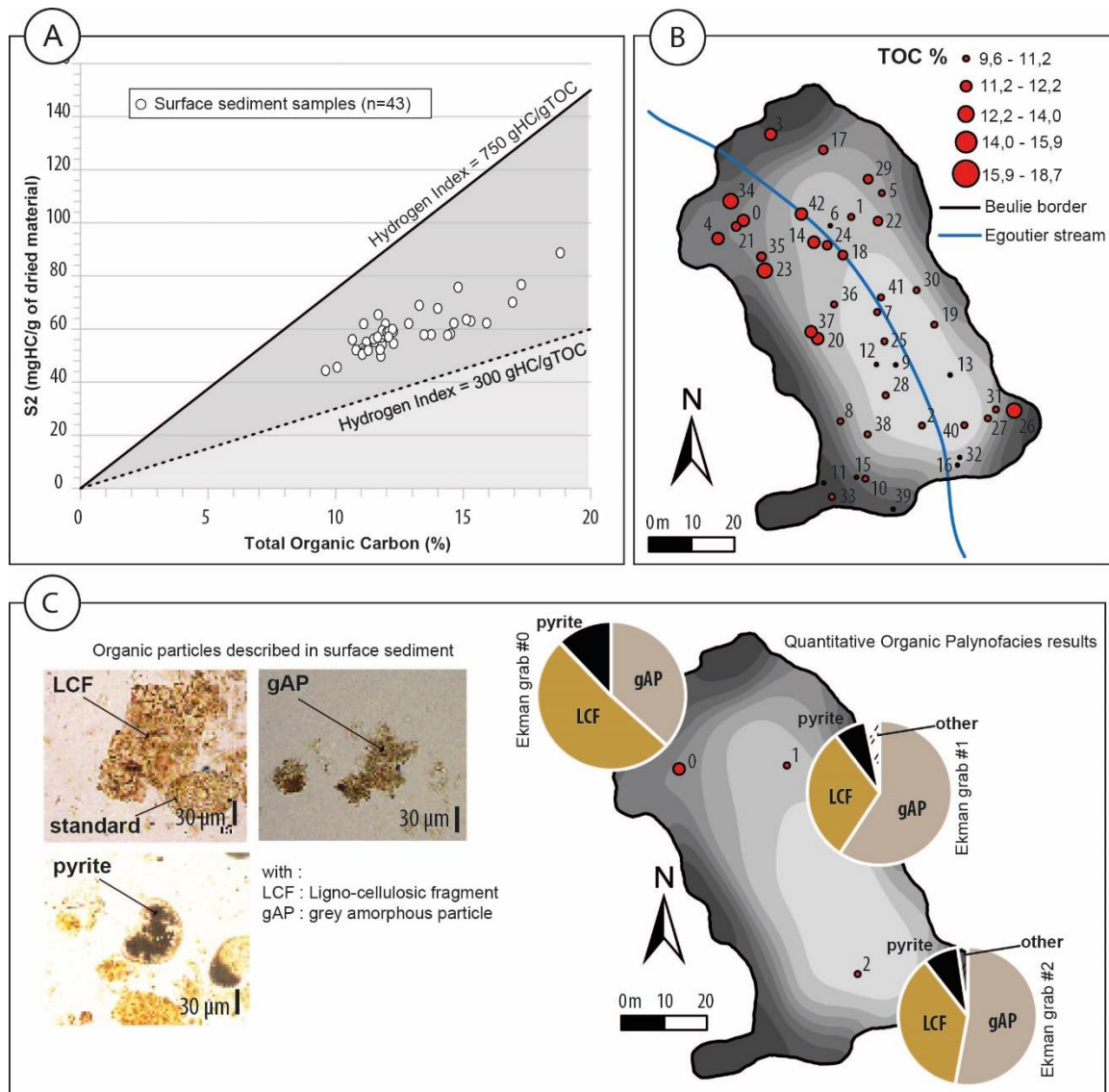


Figure 3. 2: S2 peak (mgHC/g of dried material) as a function of Total Organic Carbon (TOC, %), calculated for 43 surface sediments collected between September 2018 and September 2023 (A). Map representing the spatial distribution of TOC contents of sediment samples at the Beulie pond scale (B). Palynofacies 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).

3.1.2. Granulometric distribution

At the pond scale, and based on samples from 2021 (Figure 3.3), 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 S2.2, Figure. 3.3 A).

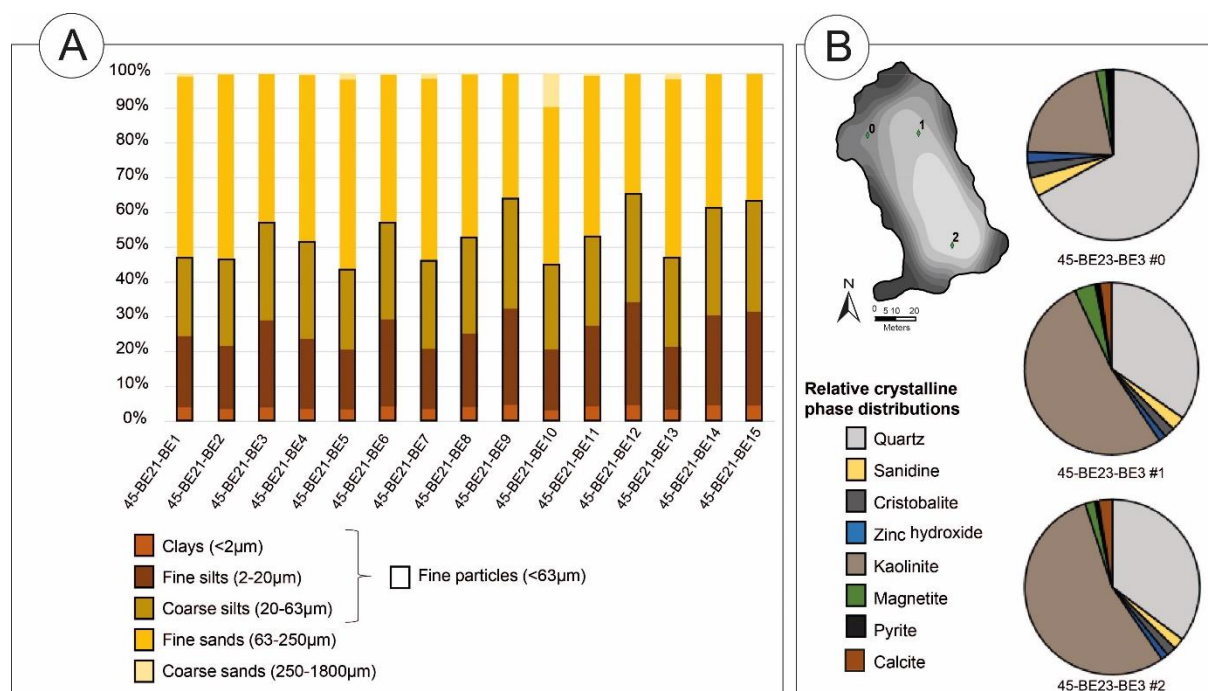


Figure 3. 3: Granulometric distribution given in % for the 15 samples collected in September 2021. (A). Relative crystalline phase distribution for the 3 bulk sediment samples collected in September 2023, including the composition in Quartz, Sanidine, Cristobalite, Zinc hydroxide, Kaolinite, Magnetite,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

3.1.3. Crystalline phase analysis

XRD analysis of surface sediment samples from three distinct pond areas (for details see Figure 3.3 B) 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) (Figure S1, Table S2.3), Specific PDF (Powder Diffraction File) card numbers for each crystalline phase are provided in Text S2.1. 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 (Figure 3.3 B–Table S2.4). 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 (Figure S2.2), while framboidal pyrite was also observed in QOC microscopy.

3.2. Pharmaceutical product distribution 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 S2.5). Spatially, their content distributions appear heterogeneous (Figure 3.4 A). 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 S2.5). These neutral PPs contents also show spatial heterogeneity at the pond scale (Figure 3.4 B). 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 trends at the pond scale (Figure S2.3).

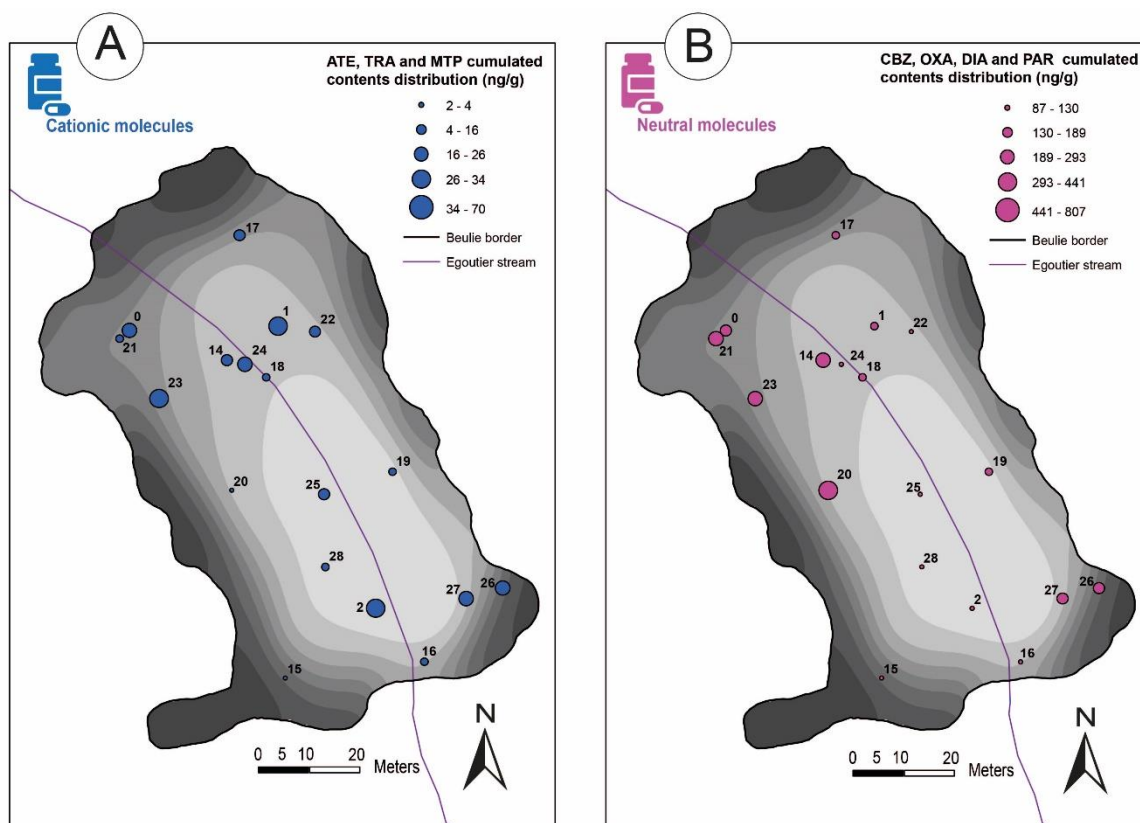


Figure 3. 4: Spatial distribution at pond scale of cumulated contents in cationic pharmaceutical products, including ATE, TRA and MTP (A). Spatial distribution at pond scale of cumulated concentration in neutral pharmaceutical products, including CBZ, OXA, DIA and PAR (B). Contents were quantified in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

4. Discussion

4.1. Bulk surface sediments 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 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 ($37.2 \pm 0.5\%$). 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 (Figure 3.5). 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.

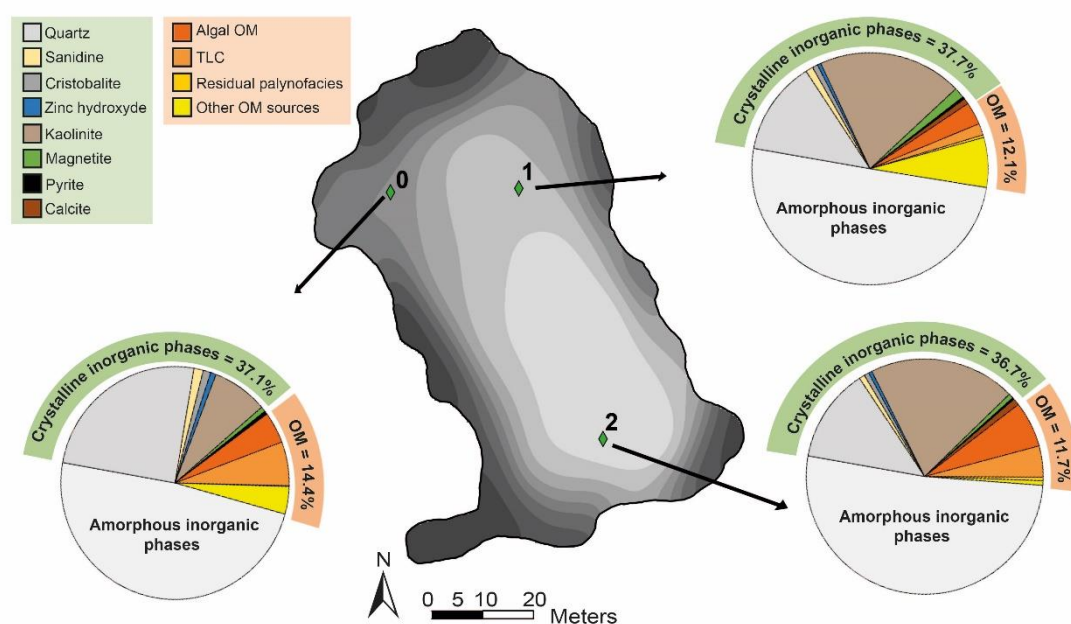


Figure 3. 5: Crystalline and organic compositions of surface sediment samples collected in September 2023 within the Beulie pond.

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 FPs, 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 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 (Figure 3.6). 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.

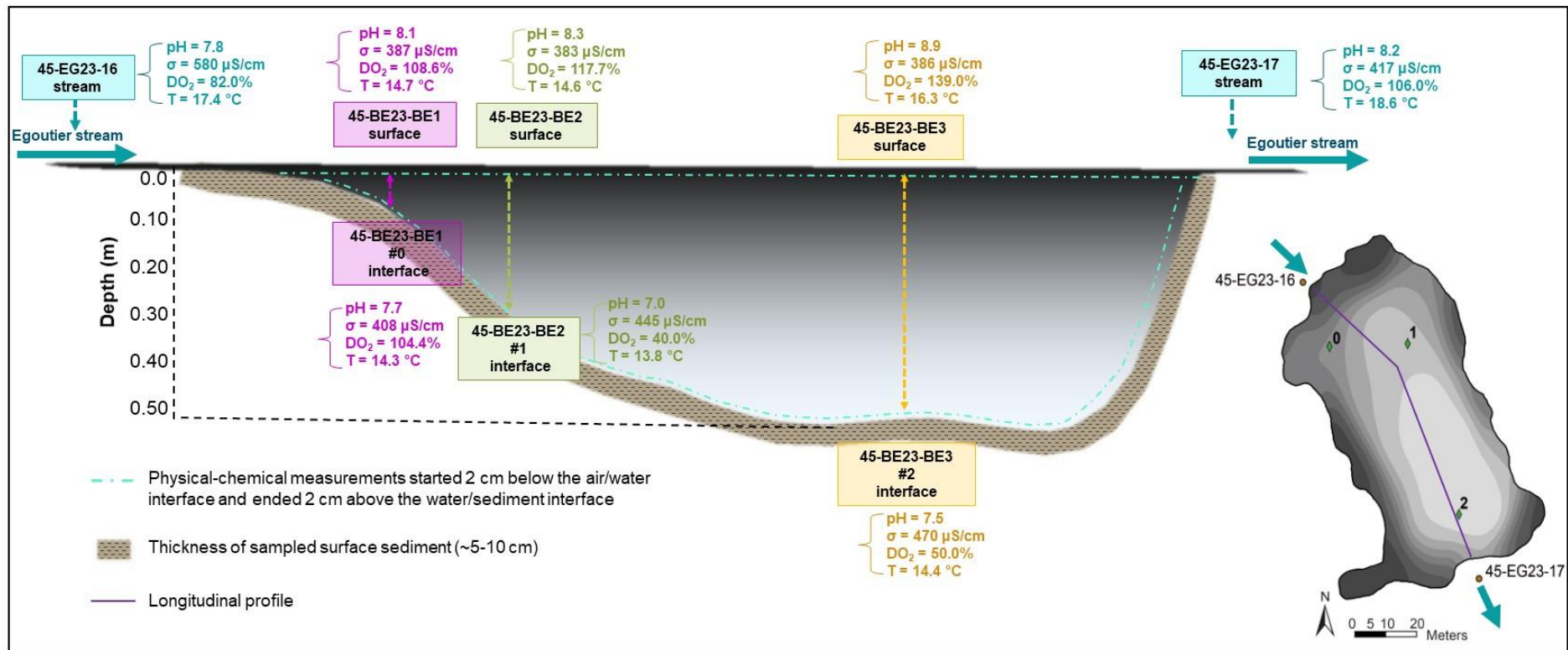


Figure 3. 6: Longitudinal profile performed from the delta to the main decantation basin of the Beulie pond. Physical-chemical measurement, including pH, electrical conductivity (σ), dissolved O_2 (DO_2) and temperature (T), were conducted in the stream at the pond's inlet (45-EG23-16), in the delta (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).

4.2.2. Organic matter dynamics in the pond

OM contents presented a heterogeneous spatial distribution at the pond scale, with a preferential accumulation in the delta, as well as differences in its palynofacies composition, depending on surface 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 O₂ concentration between the water surface and the interface in the delta, significant decrease was observed for the dissolved O₂ concentration in the main basin, when reaching the interface. The delta is very shallow (Figure 3.6), 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 products 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 logK_{ow} value, but also with its lower releasing rate through WWTPs 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 3.1). 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 (Figure 3.6). 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.

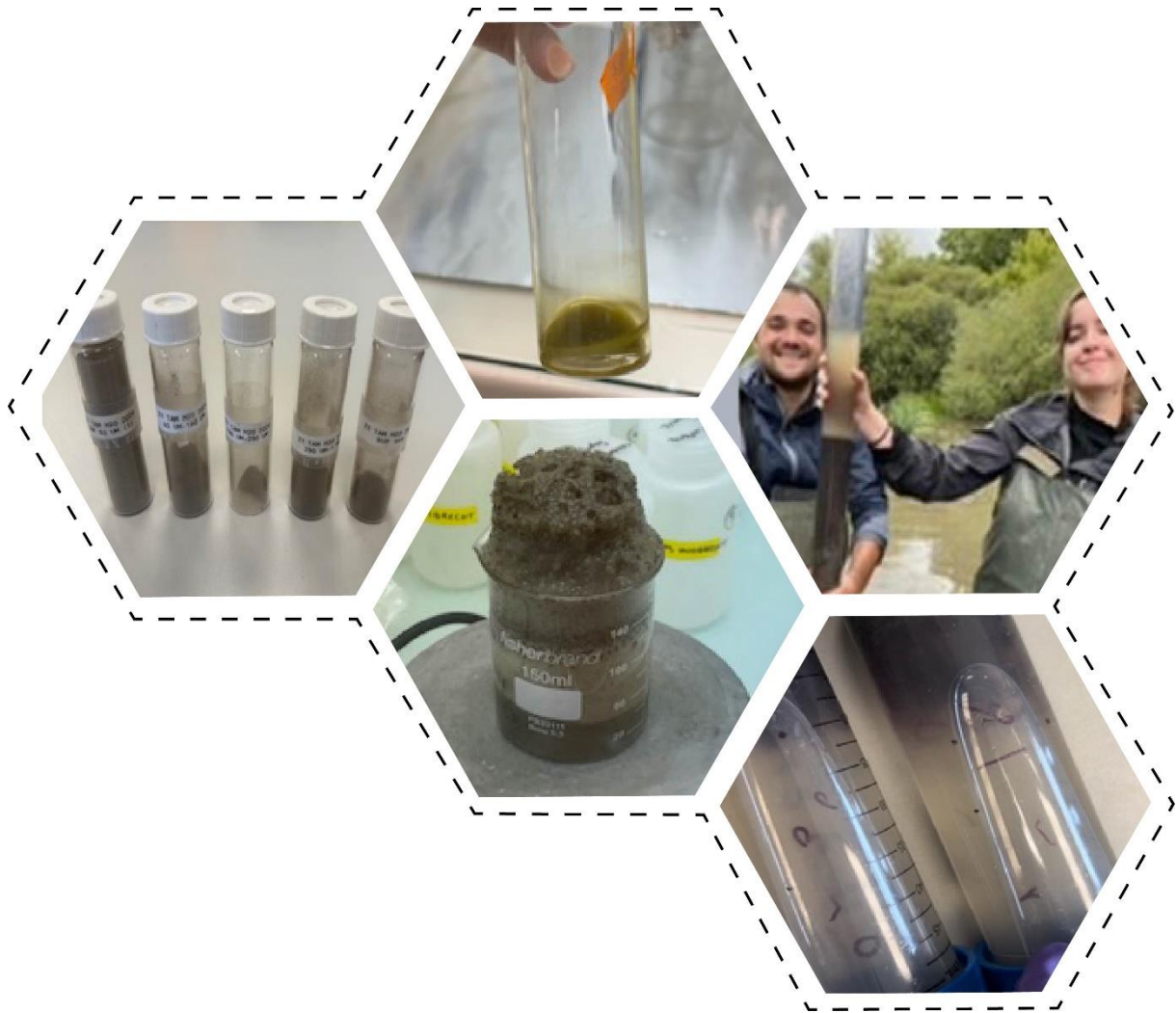
Conclusion

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 suggests 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 behaviours, in order to proceed a finer characterization of sediment components, including their content, state, and reactivity under specific physical-chemical conditions.

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Chapter 4. Pharmaceutical products in pond sediments: composition, typology and reactivity of sedimentary organic matter



The present Chapter investigates the properties of organic matter, a known and relevant potential carrying matrix of pharmaceutical products (PPs, *cf* Chapter 1 and 3), in terms of composition, typology and reactive properties, and the influence these characteristics can exercise on PPs sorption onto surface sediments. This Chapter particularly intends to examine organic matter under these various angles in different sediment grain-size fractions, the latter having different densities and settling velocities, and being potentially sentinels of different degradation state of organic matter.

The methodology presented in this work has been improved after the conclusions from a first experiment presented in Appendix 3.

The elemental characterization of organic matter was performed in the context of the internship of Clara Bruno. The preliminary calculations of organic matter relative activities were performed in the context of the Master1 internship of Alpha Ibrahima Barry.

This work is written in the form of a research article, to be submitted in Environmental Research.

The Supplementary Materials are available in Appendix 4.

Pharmaceutical products in pond sediments: composition, typology and reactivity of sedimentary organic matter

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Abstract

The fate of pharmaceutical products (PPs) bound to the particulate phase in the environment is mostly investigated in the total sediment (“bulk”) matrix, although it doesn’t consider the affinity of sediment organic and mineral solids, respectively, for PPs. The stability and the reversibility of these affinities have also been scarcely discussed. In the particular context of particulate phase accumulation within retention areas such as ponds, where sedimentary organic matter (OM), whose affinity for PPs is already well documented, is subjected to early diagenesis, this evolution questions the durability of PPs trapping onto sediments at the water/sediment interface. This study therefore examined the effect of OM composition, typology and reactive properties on PPs concentrations in different sediment grain-size fractions. Results showed a higher concentration and a better preservation of OM and higher concentrations in PPs in the coarsest (>1 mm) fraction than in the finest one (<63 µm), which is usually preferentially investigated in the literature. Results also exposed the potential reversibility of PPs trapping onto sediments, which is likely influenced by changes in the overlying water oxygenation, especially concerning neutral PPs. The FTIR characterization of OM, as well as the deconvolution of Rock-Eval S2 curves of OM allowed to identify OM fractions likely to create bonds with PPs, especially lignin and polysaccharides. The stability domains of OM in the different grain-size fractions, highlighted by a thermodynamic approach, highlighted different relative activities of the grain-size fractions regarding oxygenation conditions, which supports the influence of oxic/anoxic changes at the water-sediment interface on the stability of PPs trapping.

1. Introduction

Over the last decades, the fate of contaminants of emerging concerns in the environment, such as pharmaceutical products (PPs) has become one of the most important scientific issues in terms of environmental and human health safety (Monteiro and Boxall, 2010; Duarte et al., 2022). PPs have been studied in several compartments, such as water (Wilkinson et al., 2022), but also suspended particulate matters (da Silva et al., 2011), river bed-load sediments (Aminot et al., 2015; Ledieu et al., 2021; Le Gaudu et al., 2022) and sediments accumulated in retention areas (Larà-Martin et al., 2015; Thiebault et al., 2017, Humbrecht et al., 2025), attesting of an increasing interest for their occurrence and concentration in the particulate phase.

Studies investigating the fate of PPs bound to the particulate phase generally quantify them only in the total sediment (“bulk”) matrix (Aminot et al., 2015). The particulate phase consists in a set of organic and mineral solids and organic-mineral complexes of variable sizes, densities and reactive properties. These properties will influence both their sedimentation in retention areas such as ponds (Hossain et al., 2014; Gelhardt et al., 2021) and their ability to interact with the aqueous phase in which most of PPs are solubilized. Le Gaudu et al. (2022) and Ke et al. (2023) demonstrated the affinity between PPs and organic matter (OM), although most of PPs have a known hydrophilic character. However, the early diagenesis of sedimentary OM, driven by the properties of the hosting natural environment such as the redox potential (Boye et al., 2017), might limit or even make reversible the sorption mechanisms. Indeed, only a few studies have examined the mechanisms involved in the stability and reversibility of PPs binding to the particulate phase (Chefetz et al., 2008; Martínez-Hernández et al., 2014), and the characterization of OM is then often limited to the quantification of the total organic carbon. However, the degradation of OM controls the evolution of its surface charge and its availability in functional groups, and thus determines the bonds OM may create with charged and uncharged organic compounds. This evolution/maturation of the OM thus raises the question of the durability of the sedimentary trapping of organic compounds such as PPs.

In order to answer this question, the present study analyses jointly the distribution of PPs and of OM in the different granulometric (“grain-size”) fractions constituting sediments accumulated within the Beulie pond. The general idea is to decompose sediments in 5 grain-size fractions and to finely characterize each fraction in terms of organic composition,

typology and OM reactive properties. The objectives are more particularly to i/ determine PPs and OM contents in the 5 grain-size fractions comparatively to their contents in the total sediment (“bulk”), ii/ to discuss the effects of OM composition, typology and reactive properties in these different grain-size fractions regarding PPs distribution in these same grain-size fractions, and investigating particularly the involved chemical bonds, iii/ and to characterize the stability of PPs binding to the particulate matrix and to determine the factors likely to lead to a possible reversibility of the trapping.

2. Materials and Methods

2.1. Site description

The Beulie pond represents a surface area of about 4,000 m². The catchment area drained by the pond covers a surface area of 6.3 km² 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 two wastewater treatment plant effluents coming from the central army pharmacy and a psychiatric hospital, respectively (Figure 4.1). Previous studies conducted within the same catchment (Ledieu et al., 2020; Ledieu et al., 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 at the water/sediment interface in the Beulie pond. A recent study exposed that surface sediments from the delta of the pond were rich in OM from terrestrial origin, and concentrated in PPs, comprising CBZ, OXA, DIA, TRA and MTP notably (Humbrecht et al., 2025). This hotspot was therefore particularly investigated in the present work, in order to discuss the links between OM quantity, composition, typology and reactivity, and PPs distribution within surface sediments. The PPs investigated in the present study were CBZ, OXA, DIA, TRA, venlafaxine (VFX) and fluoxetine (FLX), because of their different physico-chemical characteristics, in particular their dissociation constant (K_a ; and $pK_a = -\log(K_a)$) and their lipophilic character expressed by their octanol-water partition coefficient ($\log(K_{ow})$). In addition, they exhibited the best analytical reproducibility among the quantified PPs.

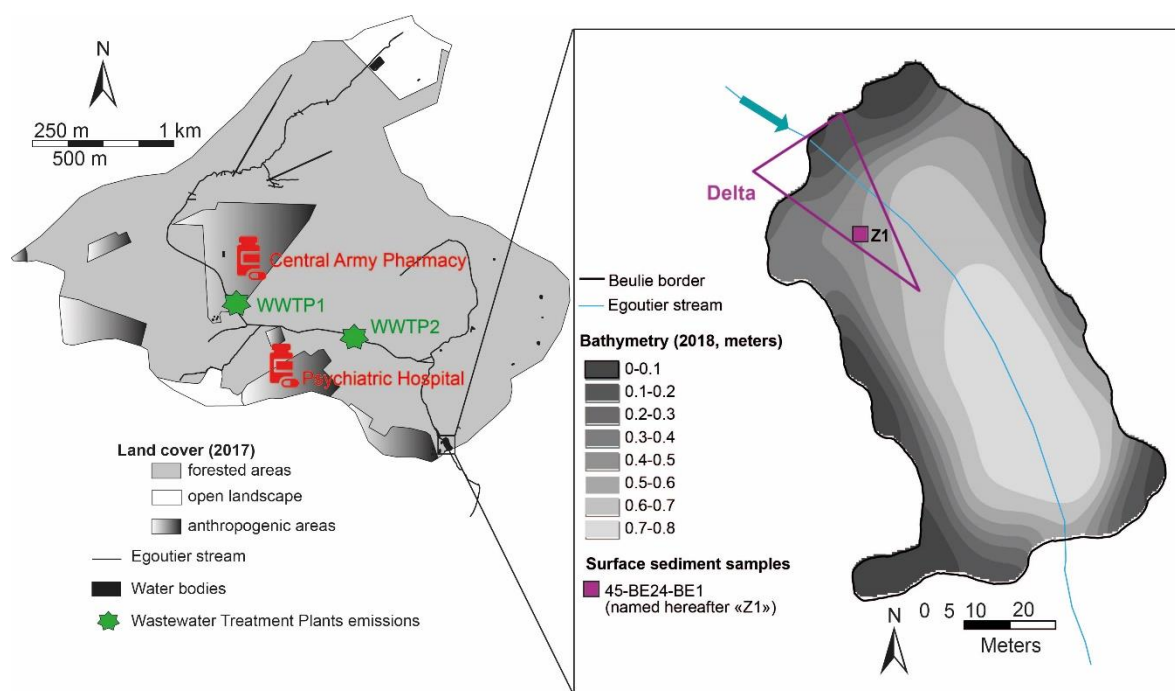


Figure 4. 1: (a) Map representing the Beulie pond catchment area with information about soil occupation collected from Corine Land Cover data from 2017. The Egoutier stream is represented by the black (catchment scale) and blue (pond scale) continuous lines. The two wastewater treatment plants connected to 1- the central army pharmacy and 2- a psychiatric hospital are represented as green stars. (b) A zoom is made on the Beulie pond. The bathymetric map is represented. The delta, represented by the purple triangle, has been identified in a previous study as a hotspot of PPs at the pond scale (Humbrecht et al., 2025), and was therefore sampled (Z1) for a further characterization of the water/sediment interface.

2.2. Sampling strategy and samples conditioning

Physico-chemical profiles were obtained at 5 cm intervals from the air/water interface to the water/sediment interface, with a continuous acquisition of pH, electrical conductivity, redox potential and dissolved oxygen. The mean value for each parameter was calculated over a 2-minutes interval.

Water samples were collected in 1 L high density polyethylene (HDPE) bottles, right above the water/sediment interface. The solution was then filtered at 0.45 μm using HVLP Membrane Durapore filters. Samples were then stored at 4 °C until analysis, excepted samples dedicated to PPs analysis, which were frozen in order to limit PPs degradation before extraction and analysis.

Surface sediment samples (i.e. sediment from a depth of 5 to 10 cm below the water/sediment interface) were also collected in several 250 mL HDPE bottles using an Ekman grab. In order to compare OM composition, typology and reactivity with PPs content in a bulk

surface sediment sample and in its different grain-size fractions, one bottle of sample was dedicated to bulk analysis and 2 bottles of samples were dedicated to two different wet-sieving procedures, one using only ultra-pure water, and the second one using only pond water collected at the water/sediment interface in the delta area. Five grain-size fractions were chosen for wet-sieving operations: >1 mm; 250 μm - 1 mm; 160 μm - 250 μm ; 63 μm - 160 μm ; and <63 μm . All samples, including bulk samples and the different grain-size fractions resulting from wet-sieving, were freeze-dried and then finely crushed in an agate mortar to ensure homogeneity, before being stored in calcinated glass vials. The sieving-waters were recovered by centrifugation of the <63 μm fraction, and were filtered at 45 μm using HVLP Membrane Durapore filters. Aliquots reserved for dissolved organic carbon (DOC) analysis were acidified at pH 2 using concentrated H_3PO_4 and stored at 4 °C until analysis, and aliquots reserved for PPs analysis were frozen until analysis.

2.3. Aqueous phase characterization

2.3.1. Dissolved organic and total nitrogen

Dissolved organic carbon (DOC) and total nitrogen (TN) were quantified using a TOC-L analyzer (Shimadzu). The day of the analysis, they were diluted by a factor 2 using ultra-pure water (MilliQ grade, 18.2 M Ω), in order to respect the device quantification ranges. The analytical sequence also included 3 blank ultra-pure water samples (filtered at 0.45 μm on the field, unfiltered also from the field and taken directly from the ultra-pure water distributor, respectively). The calibration was proceeded using calibration standards with known DOC and TN concentrations (potassium hydrogenophthalate and potassium nitrate, respectively). Moreover, inhouse standards were used as control points.

2.3.2. Pharmaceutical products

PPs were extracted from aqueous samples using Solid Phase Extraction (SPE) prior to analysis with a liquid chromatography coupled with tandem mass spectrometers (LC-MS/MS, Agilent). SPE columns were conditioned with 2x5 mL MeOH and 2x5 mL ultra-pure water prior to extraction. Then, ~200 mL of sample were used for the extraction, spiked with 50 ng of isotopically labeled internal standards. PPs were eluted from the column with 2x5 mL MeOH and finally evaporated under gentle nitrogen flow. After being reduced to ~500 μL , samples were transferred in vials and frozen until analysis.

2.4. Particulate phase characterization

2.4.1. Organic matter bulk characterization

2.4.1.1. Elemental composition

Sediment samples elemental composition was determined using elementary Flash CHNS analyzer. Sediment samples, either the bulk fraction or the five grain-size fractions, were pre-treated with hydrochloric acid (HCl) and hydrofluoric acid (HF) in order to eliminate carbonate and silicate phases from the bulk matrix, respectively, then finely crushed in an agate mortar. About 2 mg of powder were introduced in a tin capsule and analyzed in the oxidation/reduction oven, heated at a temperature reaching between 900 and 1000 °C. The oxidation of tin raised the temperature to 1800 °C, ensuring the transformation of all organic compounds into gases, including CO₂, NO₂, H₂O and SO₂. These gases are then separated thanks to a gas chromatography column, before being detected using a thermal detector. The amount of oxygen was determined by subtraction ($\%O = 100 - (\%C + \%H + \%N + \%S)$). The percentage of C, H, N, S, O were converted in %mol using the molar weight of each element (i.e. 12.01 g/mol, 1.01 g/mol, 14.01 g/mol, 32.07 g/mol and 15.99 g/mol, respectively).

2.4.1.2. Rock-Eval characterization

The Rock-Eval pyrolysis was performed on sediment samples in order to quantify and characterize their organic content and typology by thermal cracking. Analyses were carried out using Rock-Eval 6 Turbo (Vinci Technologies). The total organic carbon (TOC, in %) content and the Hydrogen Index ($HI = (S_2 \cdot 100) / TOC$ expressed in mgHC.g⁻¹TOC, 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 origin of OM in lacustrine environments (Talbot and Livingstone, 1989; Ariztegui et al., 2001; Simonneau et al., 2013b). TOC represents the amount of organic carbon in samples and HI is related to the chemical quality of the organic compounds. A decrease of the HI highlights either the oxidation of the matter in the sediment or a contribution of terrestrial material (Ramanampisoa and Disnar, 1994, Simonneau et al., 2013b).

The Rock-Eval S₂ signals were deconvoluted in order to identify the different fractions of organic matter according to their peak temperature (Hetényi et al., 2005; Sebag et al., 2006; Simonneau et al., 2013). As the number of organic matter fractions is hardly predictable, the consensus adopted in most of studies proposes a deconvolution of the signal into 4 fractions (F1 to F4), corresponding to 4 main clusters (300 – 320 °C; 360 – 380 °C; 430 – 450 °C; >470 °C), as shown by previous works (Di Giovanni et al., 1998; Noël et al., 2001; Disnar et al., 2003;

Sebag et al., 2006). The 300 -320 °C cluster is attributed to labile bio macromolecules part of plants and soil litter composition. The 360 – 380 °C cluster is attributed to resistant biopolymers like lignin and cellulose. The 430 – 450 °C cluster is attributed to humic substances and the >470 °C cluster to mature geo-macromolecules. The deconvolution was performed using Origin lab PRO, and by fixing 4 temperatures: 305.6 ± 5.4 °C, 370.2 ± 5.0 °C, 438.4 ± 8.6 °C and 483.1 ± 9.6 °C, calculated after Disnar et al. (2003), as mean values of peak temperatures of the four fractions obtained after the deconvolution of the S2 signals of podzols and spodic cambisol (n=12).

2.4.1.3. FTIR characterization

The identification of OM functional groups in the 5 grain-size fractions was determined using Fourier-Transformed InfraRed (FTIR) Spectrophotometry. To proceed so, about 300 mg of KBr salt were mixed with about 1 mg of dried sample (after the removal of carbonate and silicate phases). The mixture was finely crushed in an agate mortar, then the powder was pressed at 8 tons during 10 minutes in a hydraulic press. The resulting pellets were stored safe from humidity to limit the characteristic absorbance peak of water on FTIR spectra (Artz et al., 2008; ~ 3400 cm⁻¹).

Pellets were analyzed by mid-infrared microSpectrophotometry, using a Continuum microscope coupled to a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, USA) with an internal source (Globar). The equipments of the microscope include a liquid-nitrogen cooled 50 μ m MCT detector, a 32x infinity-corrected Schwarzschild type objective (NA = 0.65, WD = 7 mm) and a 32x condenser featured in the confocal mode. The confocal geometry was allowed by the use of the 'single aperture dual path mode'. The projected pixel size was 50x50 μ m. Each FTIR spectrum was recorded in the 4000-650 cm⁻¹ spectral range, with a resolution of 8 cm⁻¹ and 128 scans. The KBr pellet spectrum was recorded several times during the analysis, in order to consider atmospheric CO₂, CH₄ and moisture variations, and was used as background for sample pellet spectra recordings. FTIR spectra were postprocessed using OPUS 7.5 (Bruker), with baseline correction (Mozhdehei et al., 2024).

2.4.2. Pharmaceutical products

PPs were quantified using LC-MS/MS. Sediment samples were prepared and analyzed following the method described by Le Gaudu et al., (2022). Six PPs were quantified in this study: 3 positively charged PPs: TRA, VFX and FLX; and 3 PPs under neutral form: CBZ, OXA

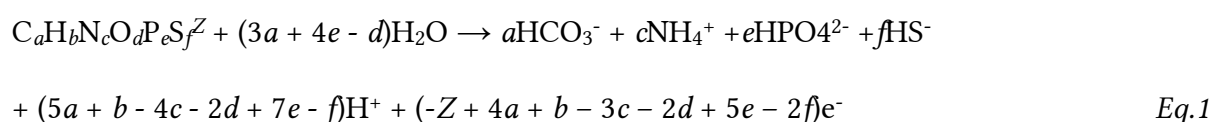
and DIA. Their characteristics at the pH range of the Beulie pond water/sediment interface (between 7.0 and 7.7 in September 2023) are given in Table 4.1. 1.0 ± 0.1 g of sample was spiked with isotopically labeled internal standards (LGC Standards), mixed with 0.5 g of EDTA and then extracted with MeOH using pressurized liquid extraction (ASE 350, Thermo) at 100°C and 1000 psi. The extract was recovered with ultra-pure water, and purified through SPE with the same protocol than aqueous samples, with an additional filtration step at 0.22 µm (Nylon filter, VWR). MeOH was used again to recover extracts, before their injection in LC-MS/MS system (Agilent). Limits of detection (LOD) and quantification (LOQ) in water and sediment are listed in Appendix 4 Table S6.4.

Table 4. 1: Physico-chemical properties of tramadol, fluoxetine, venlafaxine, carbamazepine, oxazepam and diazepam in the pH range of the Beulie pond water column. ^aThiebault et al., 2021.

Pharmaceutical products	Abbreviation	pKa ^a	Main form at Beulie pond water pH range (pH 7±1)	Log(K _{ow}) ^a
Tramadol	TRA	9.4	Cationic	3.01
Fluoxetine	FLX	9.8	Cationic	4.65
Venlafaxine	VFX	8.9	Cationic	3.28
Carbamazepine	CBZ	2.3 and 13.9	Neutral	2.45
Oxazepam	OXA	1.7 and 11.6	Neutral	3.34
Diazepam	DIA	3.4	Neutral	2.7

2.5. Organic matter thermodynamic characterization

OM thermodynamic characterization was performed by calculating the relative activity of the OM extracted from each grain-size fraction, that is its higher stability domain regarding the redox potential. This step required the calculation of the Gibbs free energy in the standard state, representing the amount of energy needed to oxidize the OM in the standard state. La Rowe and Van Cappellen (2011) evidenced a linear relationship between the Gibbs free energy and the nominal oxidation state of carbon (NOSC), calculated on the basis of the elemental composition of a variety of organic matter and organic compounds. This relationship therefore allows to calculate the Gibbs free energy with the knowledge of the OM NOSC value. The relation below gives the oxidation half reaction that determines the average oxidation state of carbon:



where a, b, c, d, e and f correspond to the stoichiometric coefficients of the elements C, H, N, O, P and S, respectively, and Z corresponds to the net charge of the organic compound. NOSC corresponds to the ration between the number of electrons exchanged and the number of carbon atoms. As the carbon in the half reaction is considered fully oxidized, meaning in the (+4) oxidation state, the NOSC is calculated as:

$$\text{NOSC} = -((-Z + 4a + b - 3c - 2d + 5e - 2f)/a) + 4 \quad \text{Eq.2}$$

The NOSC can be easily determined from the chemical formula of known organic compounds, but in the case of natural samples, the elemental composition is therefore needed.

La Rowe and Van Cappellen (2011) empirically determined the linear relationship between the free Gibbs energies and the NOSC, using organic compounds with known thermodynamic properties:

$$\Delta G_r^0 = 60.3 - 28.5 \cdot \text{NOSC} \quad \text{Eq.3}$$

At the standard state:

$$K = Q \quad \text{Eq.4}$$

with K the equilibrium constant of the half oxidation reaction, and Q the reaction quotient, which results in:

$$\Delta G_r^0 = -2.3 \cdot RT \log(Q) \quad \text{Eq.5}$$

where R designates the gas constant, equal to 8.314 J.mol⁻¹ and T the temperature in K. This relation allows to calculate Q, which also corresponds to:

$$Q = \prod (ac_i)^{\nu_i} \quad \text{Eq.6}$$

where ac_i is the activity of the specie i part of the half oxidation reaction, and ν_i corresponds to the stoichiometric coefficient of the specie i. ν_i is positive for the products and negative for the reactants. On the other hand, the electrical potential corresponding to $-\log(a_e^-)$ can be written as:

$$\text{pe} = \frac{F \cdot Eh}{2.33 \cdot RT} \quad \text{Eq.7}$$

with Eh the redox potential, R (8.314 J.mol⁻¹) the gas constant, T the temperature (298.15 K) and F the Faraday constant (96,485 C). The activity of the organic compound can therefore be calculated with Eq.7 as a function of Eh, since the pH is given and since the activities of the

other dissolved species can be estimated. However, it means that the activity of the organic compound is available in a specific environment, of known pH range and water ionic composition. The relative activity of the organic compound can also be calculated as the ratio between its activity and the sum of the activities of the other organic compounds present in the natural system.

3. Results

3.1. Water-column physico-chemical profiles

The physico-chemical profiles measured in the water-column in the delta of the Beulie pond (Figure 4.1, Table 4.1, 40 cm-depth) revealed an abrupt decrease in both redox potential (Eh) and dissolved O₂, resulting in anoxic conditions at the water/sediment interface. The pH value also slightly decreased but remained in the neutral domain, whereas electrical conductivity showed no relevant differences along the profile (Table 4.2).

Table 4. 2: Physico-chemical conditions measured in the water-column from the air/water interface to the water/sediment interface every 5 cm-depth. Measurements comprise pH, redox potential (Eh), dissolved O₂ and electrical conductivity.

Depth (cm)	pH	Eh (mV)	Dissolved O ₂ (%)	Electrical conductivity (μS/cm)
0	7.38	200	46.6	253
5	7.32	183	43.3	254
10	7.25	167	41.3	255
15	7.19	157	40.9	255
20	7.16	152	41	255
25	7.11	151	40.6	257
30	7.10	120	39.1	256
35	6.98	-6	9.6	284
40	6.94	-39	0.3	283

3.2. Organic matter patterns in the Beulie pond

3.2.1. Organic carbon grain-size distribution

For both ultra-pure water and pond water wet-sieving procedures, the grain-size fraction with the highest TOC content was the 160 μm – 250 μm fraction, reaching TOC content values of 28.7 % and 28 % respectively. The fraction with the lowest TOC content was the <63 μm fraction, reaching TOC values of 11.8 % and 11.9 %, respectively. The supra 1 mm grain-size fraction reached TOC contents of 24.3 % and 22.4 % after ultra-pure water and pond

water wet-sieving, respectively. TOC content of the 250 μm – 1 mm fraction was equal to 22.9 % with ultra-pure water sieving and 22.8 % with pond water sieving, while the 63 μm – 160 μm fraction reached TOC content of 14.1 % and 14.7 %, respectively. The two wet-sieving procedures allowed to get similar TOC content distributions, which was consistent with DOC and TN values quantified in both ultra-pure and pond sieving waters, showing negligible concentrations of OM desorbed during both wet-sieving procedures (Figure 4.2, Table 4.3).

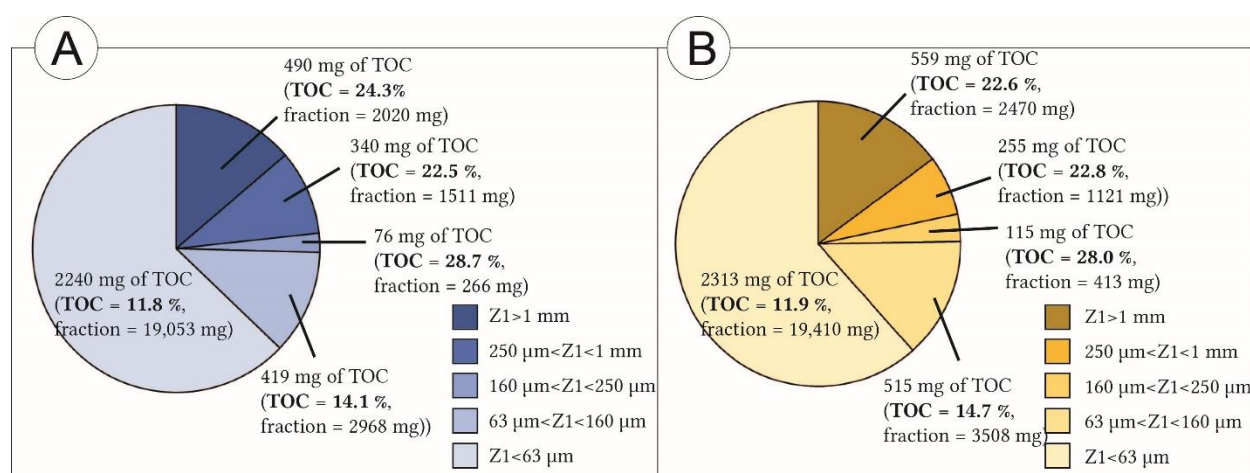


Figure 4. 2: Relative grain-size distribution of the Total Organic Carbon (TOC) content measured with Rock-eval pyrolysis and expressed in %, in the Beulie pond delta surface sediments after wet-sieving procedure using either ultra-pure water (A) or pond water (B). Combined with the mass of each grain-size fraction (expressed in mg), we also determined the amount of TOC (expressed in mg) contained in each grain-size fraction.

Table 4. 3: Dissolved organic carbon (DOC) and Total nitrogen (TN) concentrations in solutions before and after the sieving procedures done with ultra-pure water or pond water. LOD = Limit Of Detection.

	DOC before sieving (mg/L)	DOC after sieving (mg/L)	TN before sieving (mg/L)	TN after sieving (mg/L)
Ultra-pure water sieving	2.37	4.97	$\leq$ LOD	0.72
Pond water sieving	11.52	12.91	1.12	1.79

3.2.2. Particulate organic matter typology

The deconvolution of the S2 curves for both the $<63 \mu\text{m}$ and the $>1 \text{ mm}$ grain-size fractions allowed to examine the different types of organic matter that compose these two grain-size fractions. For this purpose, the temperature corresponding to the thermal cracking of the hydrocarbon compounds constituting OM were particularly studied. Whatever the water used for the wet-sieving, the F3 OM type fraction, characterized by a mean temperature of thermal cracking of 438.4°C was relatively more abundant in the $<63 \mu\text{m}$ fraction than the

F4 OM type fraction, characterized by a mean temperature of thermal cracking of 483.1 °C. The opposite trend is observed for the coarser grain-size fraction (>1 mm) (Figure 4.3).

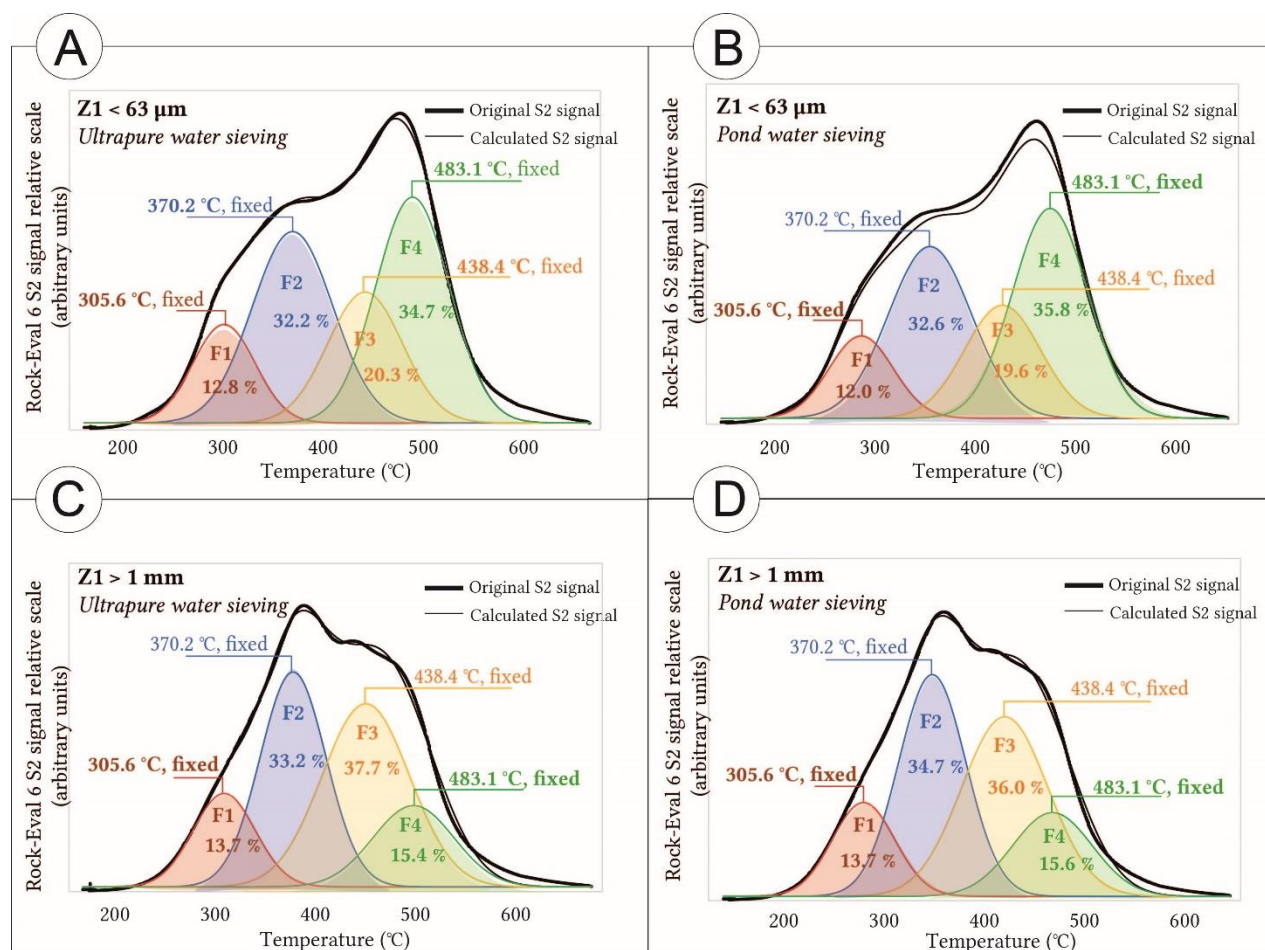


Figure 4. 3: S2 curves from Rock-Eval pyrolysis for the <63 μm fraction, recovered after ultra-pure water (A) and pond water (B) sieving, and for the >1 mm fraction, recovered after ultra-pure water (C) and pond water (D) sieving. The curves were deconvoluted into 4 main OM type fractions (F1 to F4), each characterized by a fixed peak temperature, calculated as mean values of peak temperatures obtained for the same fractions of different soil samples curves, investigated by Disnar et al. (2003).

It has to be noted that the previous digestion of carbonates and silicates allowed to avoid superimposition with bands associated with mineralogical matrices. FTIR spectra revealed very similar OM composition in functional groups between the 5 grain-size fractions, comprising mainly the OH stretching of alcohols and phenols (~3400 cm⁻¹), the symmetric and antisymmetric CH₂ related to lipids (2920 and 2850 cm⁻¹), the C=O stretch of carboxylic acids (~1715 cm⁻¹), the aromatic C=C or antisymmetric C-O stretching of COO⁻ that can be assigned to lignin (1650-1600 cm⁻¹ and 1515 cm⁻¹), the C-H deformation of phenolic and aliphatic structures (1450 and ~1375 cm⁻¹). However, only the coarsest grain-size fractions (>160 μm) spectra revealed the characteristic band of polysaccharides, structures found in plant-derived by-products and cellulose, related to the combined C-O stretching and O-H

deformation ($\sim 1050\text{-}1030\text{ cm}^{-1}$) and the C-O stretching of phenolic O-H (1266 cm^{-1}) (Cocozza et al., 2003; Artz et al., 2008; Figure 4.4).

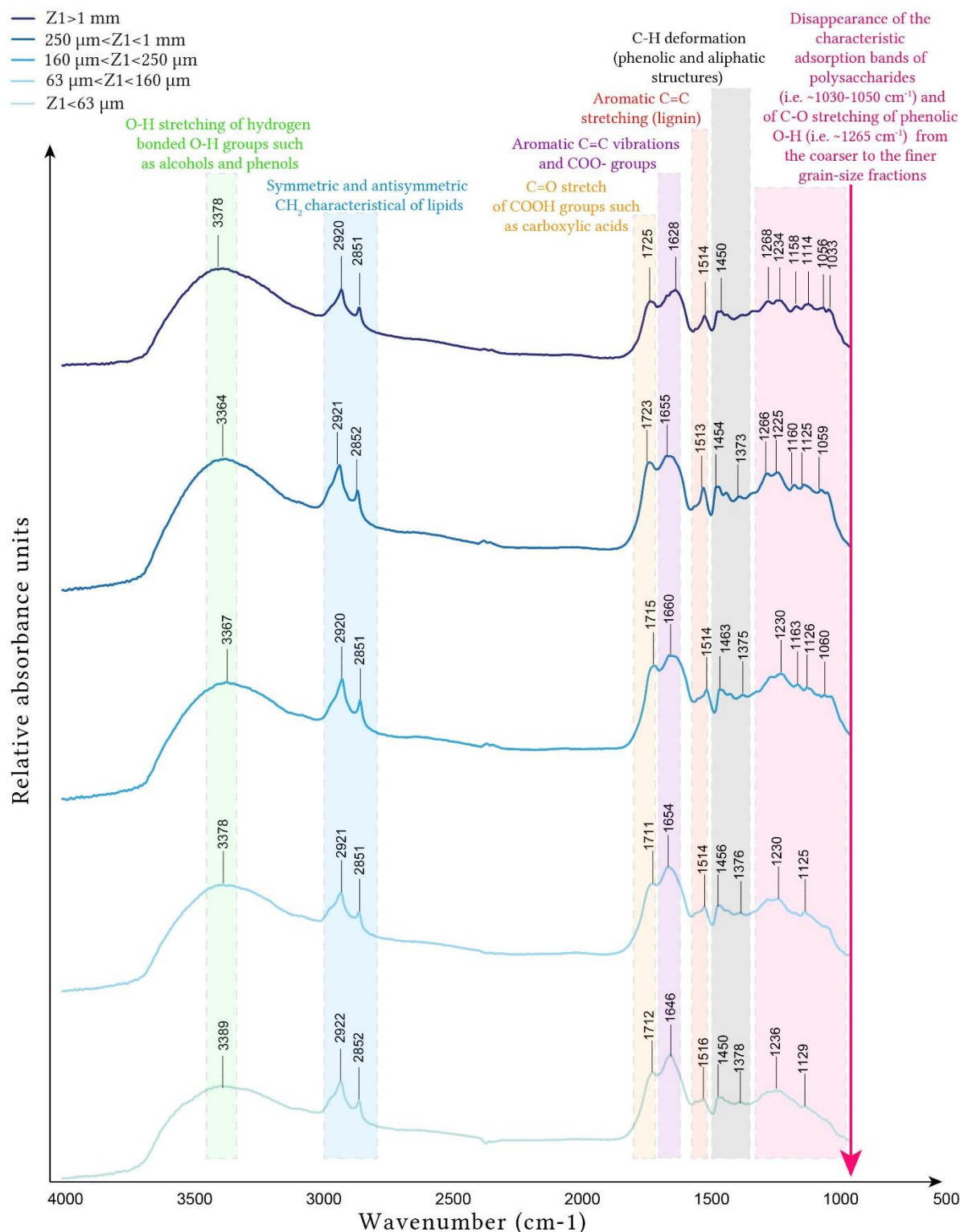


Figure 4. 4: Fourier Transform InfraRed (FTIR) Spectrophotometry spectra recorded for the organic matter contained in the 5 grain-size fractions of Z1 sample after the removal of carbonate and silicate phases by acid attacks. The functional groups are attributed to the different characteristic absorption bands in color squares, along with propositions of corresponding organic matter families, after Cocozza et al. (2003) and Artz et al. (2008).

3.2.3. Organic matter stability domains

The OM thermodynamic characterization was performed by calculating its relative activity under Eh and pH conditions such as measured at the water/sediment interface (Table 4.2). The NOSC, calculated thanks to the elemental composition of the different sediment grain-size fractions (Table 4.4), highlighted a higher oxidation state of the <63 μm fraction, with its NOSC value reaching 0.545, compared with the other grain-size fractions having slightly negative values. The relative activities of the different grain-size fractions showed that the >1 mm, 250 μm – 1 mm and the 63 μm – 160 μm fractions reached their maximal activity in less oxidizing conditions than the <63 μm fraction. The 160 μm – 250 μm fraction reached no maxima, or only in highly reductive conditions, unlikely to occur in the natural environment (Figure 4.5).

Table 4. 4: Elemental composition of OM extracted from Z1 grain-size fractions after acid attacks (HCl + HF + HCl) in C, H, N, S and O (expressed in mol%). The Nominal Oxidation State of Carbon (NOSC) was calculated after the elemental composition, and the Gibbs free energy in the standard state was calculated following the linear relationship proposed by La Rowe and Van Cappellen (2011). Log(K) was calculated in the standard state.

Samples	C (mol%)	H (mol%)	N (mol%)	S (mol%)	O (mol%)	NOSC	ΔG_r^0 (kJ/mole of C)	Log(K)
Z1>1 mm	35.8	44.6	1.35	0.44	17.8	-0.112	63.5	-25.6
250 μm <Z1<1 mm	35.2	45.0	1.92	0.64	16.8	-0.123	63.8	-25.8
160 μm <Z1<250 μm	36.1	45.7	2.11	0.66	15.5	-0.196	65.9	-26.6
63 μm <Z1<160 μm	34.7	45.6	2.31	0.66	16.7	-0.113	63.5	-25.6
Z1<63 μm	35.2	37.6	2.34	0.93	23.9	0.545	44.6	-18.0

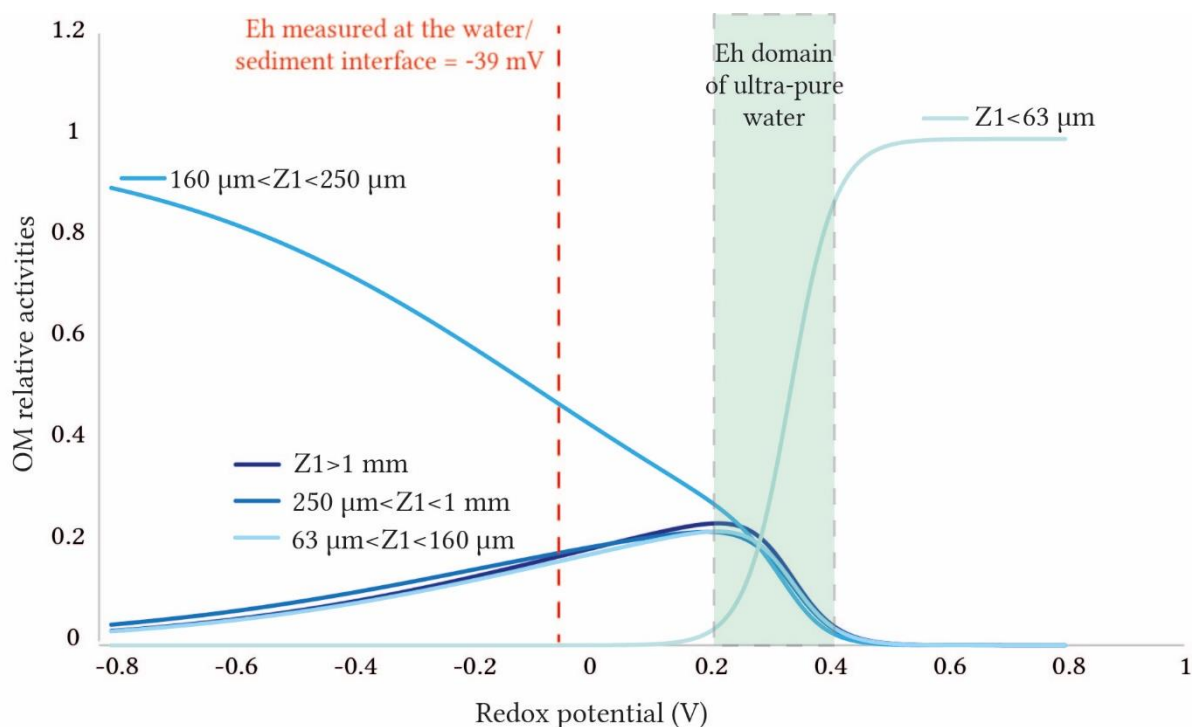


Figure 4. 5: Relative activities calculated for the OM extracted from Z1 grain-size fractions. The pH was fixed at 6.9, corresponding to the pH measured at the water/sediment interface. The redox potential measured at the water/sediment interface is represented by the red dotted line, and the redox potential domain of ultra-pure water, used for wet-sieving, is represented by the light green rectangle. Eh = redox potential.

3.3. Grain-size distributions of pharmaceutical products

3.3.1. Pharmaceutical product contents in bulk sediment and in grain-size fractions

PPs contents quantified in the bulk sediment were in average higher for carbamazepine (CBZ), oxazepam (OXA) and diazepam (DIA), the three neutral PPs under field conditions, than for tramadol (TRA), fluoxetine (FLX) and venlafaxine (VFX), the three cationic PPs under field conditions, with mean contents equal to 50.2, 233.7, 87.6, 1.8, 6.8 and 0.6 ng/g respectively. Whatever the water used for the wet-sieving, (i.e. ultra-pure or pond water), PPs were more concentrated in the coarser grain-size fraction (i.e. >1 mm) than in the finer one (i.e. <63 μm) (Figure 4.6).

- Z1>1 mm (pond water sieving)
- Z1<63 μ m (pond water sieving)
- Z1>1 mm (ultra-pure water sieving)
- Z1<63 μ m (ultra-pure water sieving)
- Bulk Z1

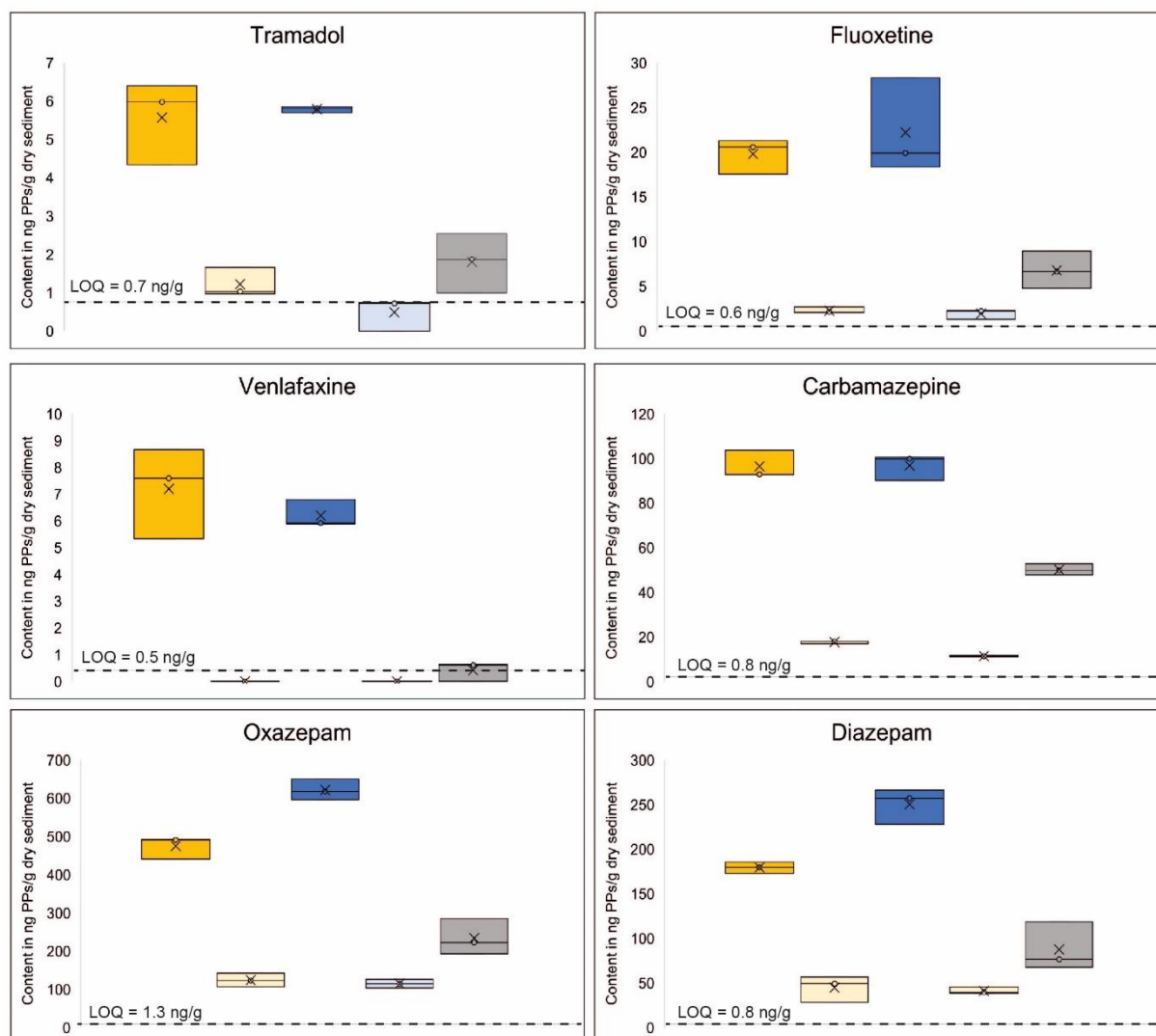


Figure 4. 6: Concentrations in PPs, including tramadol (TRA), fluoxetine (FLX), venlafaxine (VFX), carbamazepine (CBZ), oxazepam (OXA) and diazepam (DIA) in the >1 mm fraction, the <63 μ m fraction and the total fraction. Boxplots represent triplicate concentration results. LOQ = Limit Of Quantification.

3.3.2. Pharmaceutical product contents in water samples collected after wet-sieving

PPs content were also quantified in the water samples collected after wet-sieving procedures, by centrifuging the <63 μ m grain-size fraction (5 minutes at 10,000 g, Figure 4.7). Concerning TRA and VFX, the total mass quantified in the water after wet-sieving was lower compared with the one quantified in the “initial” pond water used. With the ultra-pure wet-sieving, no difference was observed. FLX was not quantified in the dissolved phase, whatever

the water used for wet-sieving. Concerning CBZ, OXA and DIA, their total mass was higher in the water collected after wet-sieving procedures, whatever the water used. However, the difference in mass was higher when using ultra-pure water than pond water for the wet-sieving procedure.

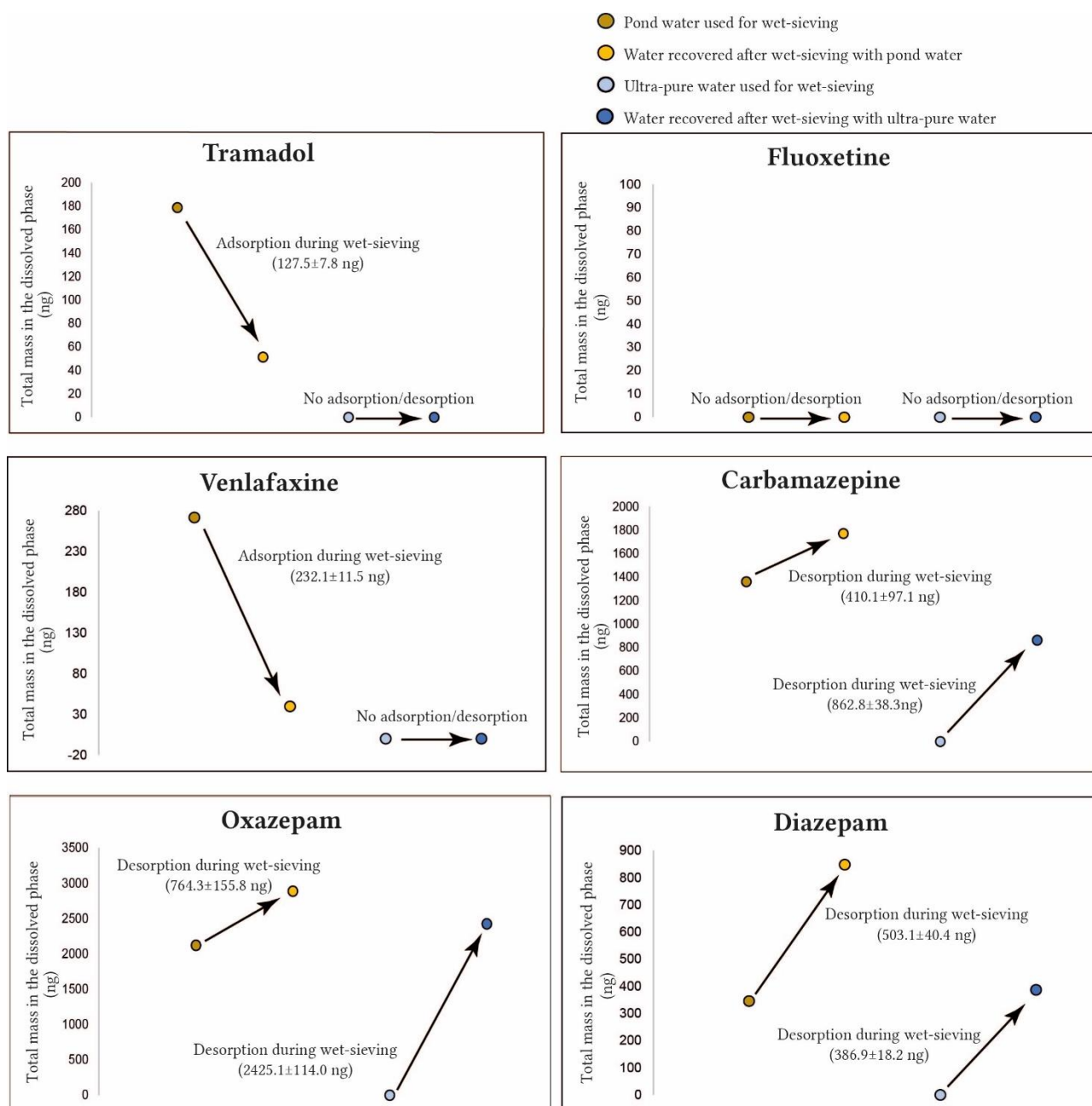


Figure 4. 7: PPs mass in the pond water volume used for wet-sieving and in the sieving-water volume recovered, and PPs quantified in the sieving-water volume recovered after wet-sieving using ultra-pure water. PPs mass in the ultra-pure water volume were assumed to be null. Arrays represent either PPs adsorption onto the particulate phase or desorption from the particulate phase during wet-sieving.

4. Discussion

4.1. The grain-size distribution of PPs concentrations: insights provided by OM typology

Surprisingly, the grain-size distribution of PPs concentrations in surface sediments revealed a higher concentration of PPs in the coarsest fraction (i.e. >1 mm) than in the finest one (<63 μm). Indeed, the coarsest grain-size fraction is not usually preferentially investigated in the literature when the fate of PPs adsorbed onto the particulate phase is studied, since its specific surface area is limited compared with that of the finest grain-size fraction (Le Gaudu et al., 2022). Furthermore, clay minerals are part of the finest fraction, and constitute a known reactive matrix for the adsorption of PPs (Hounfodji et al., 2021). Indeed, a previous study particularly highlighted the presence of kaolinite in Beulie pond surface sediments (Humbrecht et al., 2025). Since OM was found to be an important component of surface sediments (Figure 4.2), its typology was here further investigated. The hydrogen index (HI) parameter was found to be higher in the coarsest than in the finest grain-size fraction (Appendix 3, Table S3.1), suggesting a higher freshness of the OM in the coarsest grain-size fraction, which is consistent with a lower degradation of the OM (Simonneau et al., 2013b), and thus with a better preservation of its functional groups. FTIR results confirmed the presence of OM functional groups, especially O-H groups, carboxylic groups, phenolic groups and polysaccharides. The deconvolution of Rock-Eval S2 curves revealed that F3 (i.e. mean temperature of thermal cracking 438.4 $^{\circ}\text{C}$, Figure 4.3) appeared to account for a larger proportion of the >1 mm fraction, whereas F4 (i.e. mean temperature of cracking of 483.1 $^{\circ}\text{C}$, Figure 4.3) accounted for a larger proportion of the <63 μm fraction. This suggests that the >1 mm fraction would be essentially composed of humic substances (marked by F3), known to be highly functionalized, and containing especially carboxylic and phenolic groups (Tardy et al., 1997); while the finer fraction (<63 μm) would be mainly composed of mature geo-macromolecules (Sebag et al., 2006), also referred to as refractory geo-macromolecules (Czirbus et al., 2016) (i.e. F4). Furthermore, FTIR results highlighted the disappearance of polysaccharides-like absorbance bands (Figure 4.4), such as typically cellulose, from the coarsest to the finest grain-size fraction, which is consistent with the results published by Humbrecht et al. (2025) demonstrating that sedimentary OM in the Beulie pond delta was mainly of terrigenous origin represented by plant residues.

Liu et al. (2021) have demonstrated the very stable adsorption capacity of cellulose under a wide range of pH conditions in the water, and Xu et al. (2025) have exposed the high functionalization of polysaccharides, allowing them to create bonds with other compounds, and their use as drug carriers in medicine, due to their good adsorption capacity for such organic molecules, and their stability under pH variations. These properties of the coarsest grain-size fraction suggest a greater capacity to carry organic compounds such as PPs compared to the finest fraction. TRA, FLX and VFX, since they are positively charged, are likely to create electrostatic interactions with OM negatively charged functional groups, such as carboxylic and phenolic groups (Park et al., 2018). FLX was not quantified in the dissolved phase, supporting a stronger affinity for the particulate phase, a result already observed by Bernier-Turpin et al. (2025). Furthermore, FLX has a high lipophilic character ($\text{Log}(K_{ow}) = 4.65$, Table 4.1), which supports its affinity for lipids for example. Under neutral form, CBZ, OXA and DIA are more likely to create hydrophobic interactions with OM (Park et al., 2018), and one of the characteristics of these interactions is their reversibility (Grzelczak and Liz-Marzán, 2014), which is consistent with the desorption of CBZ, OXA and DIA from sediments during both wet-sieving procedures.

4.2. Physico-chemical conditions: a gateway to reversible processes?

The results of the quantification of PPs in the waters used for and recovered after wet-sieving procedures suggest an adsorption of TRA and VFX onto sediment and a desorption of CBZ, OXA and DIA from sediment during the wet-sieving. No changes were observed concerning FLX since the latter was not detected in the dissolved phase. An explanation of TRA and VFX adsorption and CBZ, OXA and DIA desorption might be the variations of physico-chemical properties of the waters used for wet-sieving compared with the water at the water/sediment interface of the Beulie pond. The pH of pond water during sieving was of 7.5, while the pH of ultra-pure water is generally between 1 and 2 pH units below 7. Regarding the respective pKa of TRA, FLX, VFX, CBZ, OXA and DIA (Table 4.1), this range of pH change is not likely to affect the form they initially had at the water/sediment interface (positively charged for TRA, FLX and VFX and neutral form for CBZ, OXA and DIA). Pond water and ultra-pure water are also both highly oxygenated compared with water at the water/sediment interface, depleted in dissolved O₂ (Table 4.2), illustrating oxic conditions during the wet-sieving and anoxic conditions at the water/sediment interface, and an anoxic/oxic transition

is likely to affect OM thermodynamic preservation (Boye et al., 2017). Indeed, the OM contained in the coarsest fraction presents a higher relative activity than the one contained in the finest fraction, at the Eh value measured at the water-sediment interface ($E_h = -39$ mV), suggesting a higher stability of the coarsest fraction than the finest one under anoxic conditions. The wet-sieving procedures induced a reoxygenation of water, and in the Eh domain of ultra-pure water, the coarsest fraction is reaching its maximal relative activity, and then its minimum, and inversely for the finest one (Figure 4.5). This prevents from determining the grain-size fraction that was originally carrying the PPs quantified in the waters collected after the wet-sieving procedure. However, as PPs concentrations were still higher in the coarsest grain-size fraction than in the finest one, it supports the hypothesis that the coarsest fraction was less impacted than the finest one by the wet-sieving procedure.

Oxic conditions are also likely to occur at the water/sediment interface. Indeed, they were observed at the water/sediment interface in September 2023 (Humbrecht et al., 2025), thus suggesting a possible desorption of PPs from sediments also in the natural environment. The degradation of OM has been shown to depend heavily on the availability of terminal electron donor (TED) and acceptors (TEA) (Sutton-Grier et al., 2011). Indeed, competition may occur, with OM being preferentially consumed when offering the higher energy yield to decomposers, and which highlights a thermodynamic control on OM degradation depending on whether the conditions are oxic or anoxic (Boye et al., 2017; Zheng et al., 2024). This shows the significant impact of oxic conditions at the water/sediment interface, since this process influence the availability in TEA and TED, as well as the preferential degradation and/or preservation of OM, directly linked to its functionalization and thus to its capacity to create or conserve bonds with PPs.

Conclusion

The present study allowed to identify differences in terms of OM composition, typology and reactivity among surface sediment grain-size fractions, and showed also a heterogeneous distribution of PPs concentrations in these grain-size fractions, with highest concentrations reached in the coarsest grain-size fraction (i.e. >1 mm). The extensive characterization of OM particularly highlighted the presence of polysaccharides-like compounds in the coarsest grain-size fraction, likely to contribute to the capacity of OM to carry PPs. The wet-sieving procedures employed to isolate the different grain-size fractions ended in the desorption of neutral PPs (CBZ, OXA and DIA) from sediment and the adsorption

of cationic PPs (TRA and VFX) onto sediment. The physico-chemical characteristics of PPs, especially their charge and their octanol/water partition coefficient ($\text{Log}(K_{ow})$), coupled with the reactivity of OM provided insights on both the potential bonds between PPs and OM functional groups, and the potential reversibility of PPs trapping onto sediments when the oxygenation conditions at the water/sediment interface vary. This work therefore demonstrated i/ the role played by OM composition, typology and reactivity, more than its content in sediments, ii/ the role played by PPs intrinsic physico-chemical properties on their ability to create bonds with OM functional groups, and iii/ the potential reversibility of adsorption processes in the natural environment as a function of physico-chemical conditions occurring in the natural environment as well as OM degradation or preservation state.

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Chapter 5. What are the factors driving the stability of PPs trapping within surface sediments and its potential reversibility?



Chapter 5 constitutes a preliminary experimental approach that aims to explore the sorption/desorption kinetics of pharmaceutical products (PPs) onto the particulate phase, in relation to the stability/reversibility of their trapping onto surface sediments. Furthermore, this chapter compares the adsorption of PPs onto a complex matrix such as surface sediment in comparison with a “simple” matrix like kaolinite. Moreover, this chapter intends to examine the potential interactions and synergy existing between surface sediments reactive matrices, in particular organic matter and clay minerals, and the influence this complexity can have on the trapping of PPs.

The supplementary materials are available in Appendix 6.

1. Introduction

According to the literature introduced in Chapter 1, and supported by the results obtained from Chapters 3 and 4, the sorption of pharmaceutical products (PPs) onto sediments has been found to be driven both by intrinsic characteristics of PPs, such as their charge, and partition coefficients (K_{ow} = octanol/water partition coefficient; K_{oc} = organic carbon partition coefficient), and by sediments characteristics, namely their clay and organic carbon (OC) content (Al-Khazraji and Boxall, 2016). Furthermore, Chapter 4 exposed the characteristics of organic matter (OM) likely to influence its ability to bind to PPs, which are not limited to the single OC content. Indeed, the composition of OM in functional groups and its reactivity within sediment grain-size fractions were found to play a key role in PPs concentration distributions within these grain-size fractions.

Behara et al. (2010) and Liu et al. (2020) also pointed the influence of environmental factors, such as pH and ionic strength, on the capacity of PPs and sediments to create bonds, and on the stability of such interactions. Moreover, Chapter 4 particularly highlighted the sorption or desorption of PPs from sediments during the wet-sieving procedures. A hypothetical factor was the oxidative character of waters (ultra-pure or pond waters) used for the procedure, while the oxygenation of the water at the water/sediment interface was close to 0% dissolved O_2 , and the redox potential was negative (-39 mV), which is characteristic of anoxic conditions.

2. Experimental approach

This chapter therefore proposes to investigate the sorption onto or desorption from surface sediments of 6 PPs, including carbamazepine (CBZ), oxazepam (OXA) diazepam (DIA), paracetamol (PAR), tramadol (TRA) and diclofenac (DIC). This section aims to evaluate more particularly the stability of PPs bonds with sediments under changes of physico-chemical conditions, and consequently to question the reversibility of the PPs-sediment and PPs-pond water interactions, considering particularly the kinetics of these interactions. To proceed so, a kinetic experiment was carried on, which consisted in the stirring of wet bulk surface sediment with water collected at the water/sediment interface, with regular sampling of the aqueous phase in order to quantify PPs. The complete experimental setup is described in Chapter 2, Section 8.1.

This chapter also compares the adsorption of PPs onto one natural solid phase that is dry bulk surface sediments, and to one “pure” solid phase that is kaolinite. This clay mineral was chosen because of its known affinity for PPs (*cf* Chapter 1) and because it is part of the natural composition of sediments. The aim is more particularly to determine if the complexity of natural sediments in terms of composition plays a role on the adsorption of PPs. It more precisely intends to determine if the adsorption of PPs onto bulk sediments is driven only by their composition and content in carrying matrices (OM, clay minerals), or also by synergistical interactions between these carrying matrices. To proceed so, batch experiments were carried on, with the solid phase being either dry bulk surface sediments or kaolinite or a mix of both phases. The referenced material Kaolinite KGa-2 (Clay Mineral Society) was chosen on this purpose. The aqueous phase was a solution of either CBZ or TRA, 2 PPs with different charges, CBZ being neutral and TRA cationic in the pH range of the Beulie pond (pH between 6 and 8) and of the experiment (pH between 4.5 and 6.5, no buffer was used). The complete experimental setup is described in Chapter 2, Section 8.2.

3. Results

3.1. Sorption/desorption kinetic experiment

The physico-chemical parameters measured at each sampling step of the sorption/desorption experiment showed a decrease in pH from 7.9 to 7.5 within the first 10 minutes of the experiment, fluctuations in electrical conductivity within a range of 37 $\mu\text{S}/\text{cm}$, as well as in dissolved O_2 within a range of 8.5 %. Furthermore, the redox potential decreased from 249 to 218 mV between the beginning and the end of the experiment (Table 5.1).

Table 5. 1: Physico-chemical parameters, including pH, electrical conductivity, dissolved oxygen and redox potential, measured at each sampling step during the sorption/desorption kinetic experiment.

Sampling steps	pH (pH units)	Electrical conductivity ($\mu\text{S}/\text{cm}$)	Dissolved O_2 (%)	Redox potential (mV)
0 min	7.9	254	108	249
10 min	7.6	291	100	241
30 min	7.5	279	106	239
60 min	7.5	277	105	218

The quantification of PPs concentrations in the dissolved phase at each sampling step highlighted that CBZ concentration increased by 70 ng/L during the first 10 min of stirring before reaching an asymptote. OXA and DIA concentrations increased as well, by 110 ng/L

after 30 min and 70 ng/L after 60 min for OXA, and by 45 ng/L after 10 min and 20 ng/L after 60 min for DIA. Inversely, both PAR and TRA contents decreased of 27 ng/L after 10 min of stirring. Finally, DIC content firstly decreased by 14 ng/L after 30 min of stirring, then increased by 26 ng/L after 60 min (Figure 5.1).

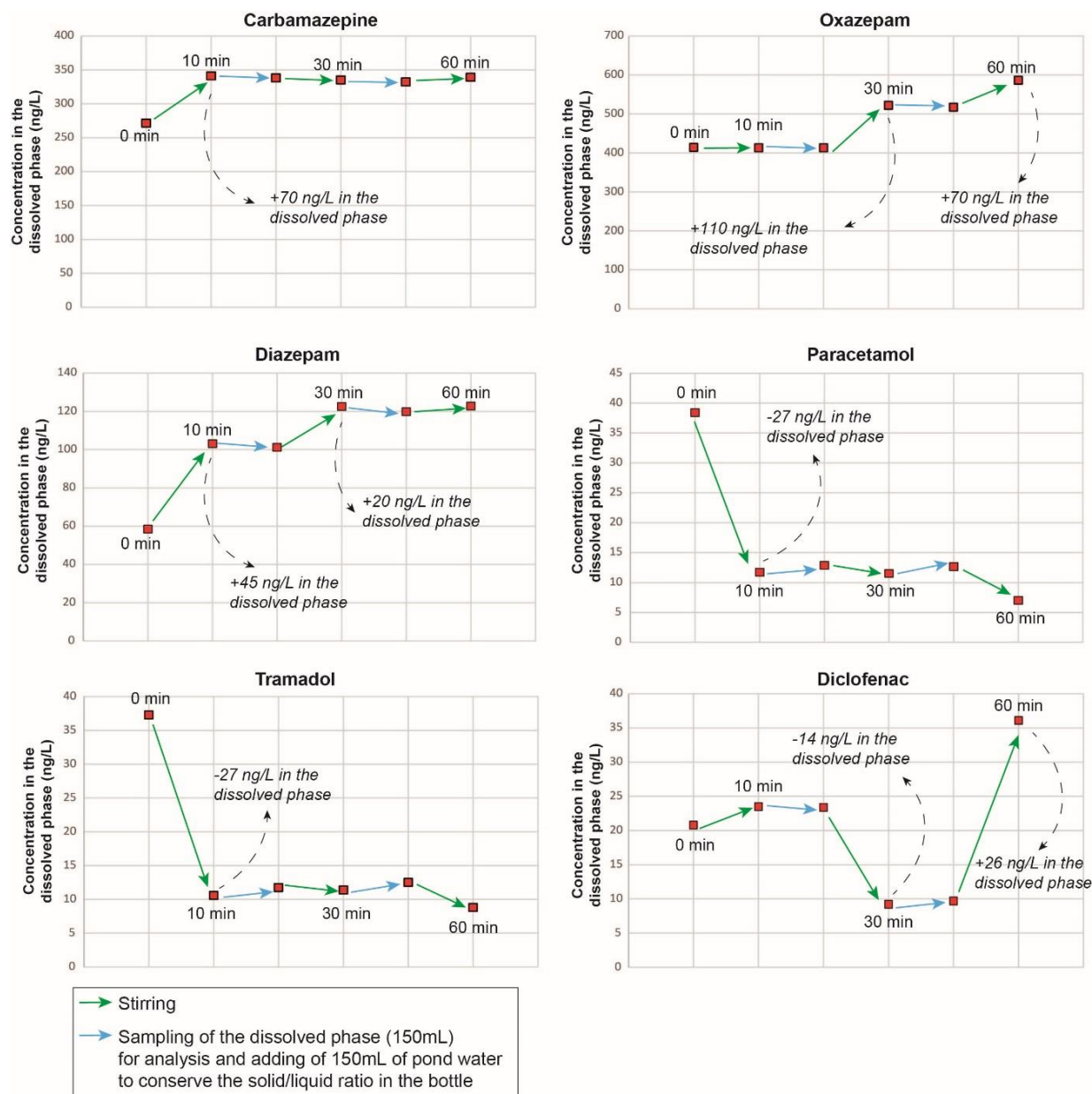


Figure 5. 1: Evolution of PPs concentration, including carbamazepine (CBZ), oxazepam (OXA), diazepam (DIA), paracetamol (PAR), tramadol (TRA) and diclofenac (DIC) in the dissolved phase as a function of time of stirring. At 0 min, the dissolved phase corresponds to pond water. At 10 min and 30 min, an aliquot of 150 mL was sampled for PPs quantification, and 150 mL of pond water were added to conserve the liquid/solid ratio.

3.2. Sorption batch experiment

3.2.1. PPs concentration in the dissolved phase at equilibrium

The quantification of CBZ and TRA concentrations in the dissolved phase of batch samples at equilibrium revealed that both PPs were partially adsorbed onto the solid phase, regardless of its composition (bulk sediment only, kaolinite only or 75 wt% bulk sediment/25 wt% kaolinite). Both PPs presented a higher sorption onto surface sediment than onto kaolinite alone. Indeed, surface sediment adsorbed in average 25 % more than kaolinite in the case of CBZ, and 39 % more in the case of TRA. In the case of CBZ, the adsorbed concentration onto the solid phase composed of 150 mg of surface sediment and 50 mg of kaolinite was similar to the one onto surface sediment alone, while in the case of TRA the adsorbed concentration onto the mixed phases was lower than the one onto surface sediment alone (Figure 5.2).

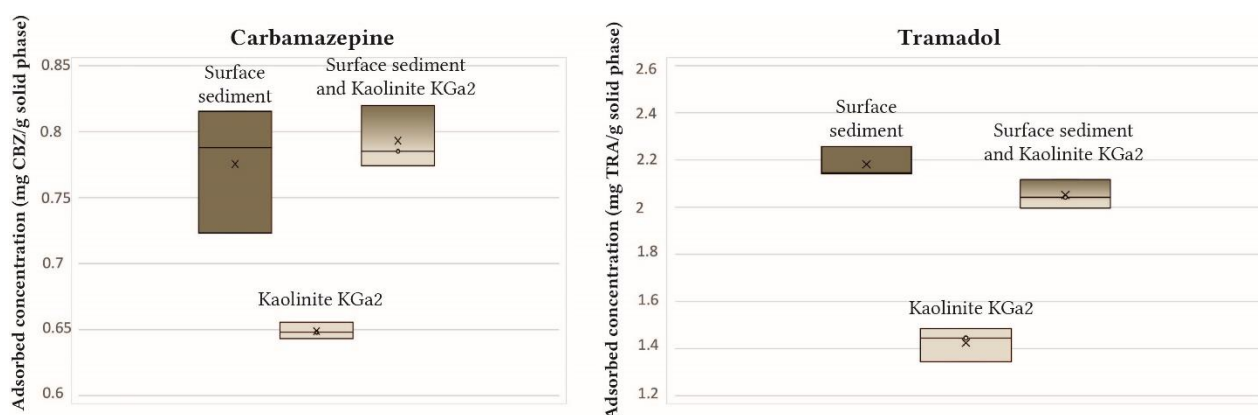


Figure 5. 2: Adsorbed concentration of carbamazepine (CBZ) and tramadol (TRA) onto 3 different solid phases: Beulie pond surface sediment (dried, 200 mg), kaolinite KGa2 (200 mg) and a mix of surface sediment (150 mg) and of kaolinite KGa2 (50 mg). The concentrations are expressed in mg PPs/g solid phase. Sorption batch experiments were performed in triplicate.

The pH measured at equilibrium remained closed to neutrality when Beulie pond surface sediment was part of the solid phase. In the case of kaolinite alone as solid phase, the pH decreased, reaching 4.5 (Table 5.2).

Table 5. 2: Blank samples and carbamazepine/tramadol batch samples pH measured at equilibrium.

		pH at equilibrium
Blank samples	Blank-Beulie	6.5
	Blank-Kaolinite	4.5
	Blank-Beulie+Kaolinite	6.5
CBZ Batch samples	Batch-Beulie-CBZ	6.5
	Batch-Kaolinite-CBZ	4.5
	Batch-Beulie+Kaolinite-CBZ	6.4
TRA Batch samples	Batch-Beulie-TRA	6.5
	Batch-Kaolinite-TRA	4.5
	Batch-Beulie+Kaolinite-TRA	6.5

3.2.2. Functional groups of the solid phase with and without sorption

The FTIR spectra of batch and blank samples solid phases showed no evolution in the composition in functional groups before and after the interaction with CBZ and TRA solutions (Figure 5.3). The functional groups identified in the case of Beulie pond sediments blank sample comprised mainly OH stretching ($\sim 3400\text{ cm}^{-1}$), symmetric CH_2 (2920 cm^{-1}), aromatic $\text{C}=\text{C}$ vibrations and COO^- group ($1640\text{--}1650\text{ cm}^{-1}$), according to Cocozza et al. (2003) and Artz et al. (2008). The absorption band at $1030\text{--}1050\text{ cm}^{-1}$ is possibly related to inorganic compounds, such as quartz or other minerals, part of surface sediments composition (Humbrecht et al., 2025), although it is difficult to clearly attribute these bands to one specific matrix, regarding the heterogeneity of sediments. In the case of kaolinite blank sample, the main functional groups were attributed to the OH stretching bands (3620 , 3653 , 3697 and 915 cm^{-1}), and the Si-O stretching bands (1100 , 1030 , 1010 , 795 , 755 and 695 cm^{-1}), according to Johnston et al. (2008) and Nazdracheva et al. (2022). In the case of the blank sample of the mix (75 wt% bulk sediment/25 wt% kaolinite), both sediments and kaolinite functional groups were identified on the spectrum, with a superposition of bands (Figure 5.5). After the interaction of PPs with the solid phases, no new absorption bands appeared on spectra (Figure 5.3 to 5.5).

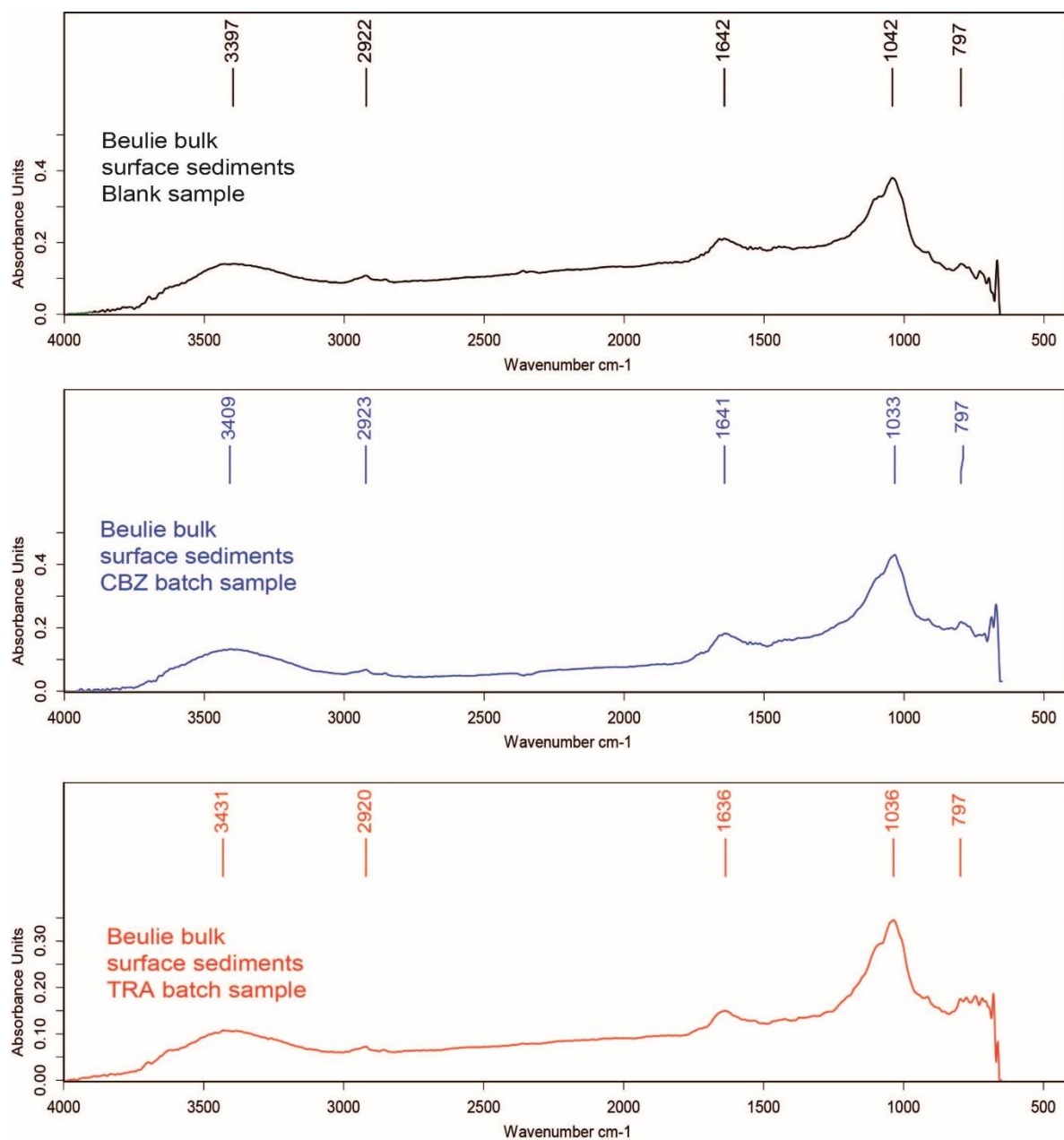


Figure 5. 3: FTIR spectra of Beulie surface sediments samples: blank (in black), CBZ batch (in blue) and TRA batch (in red).

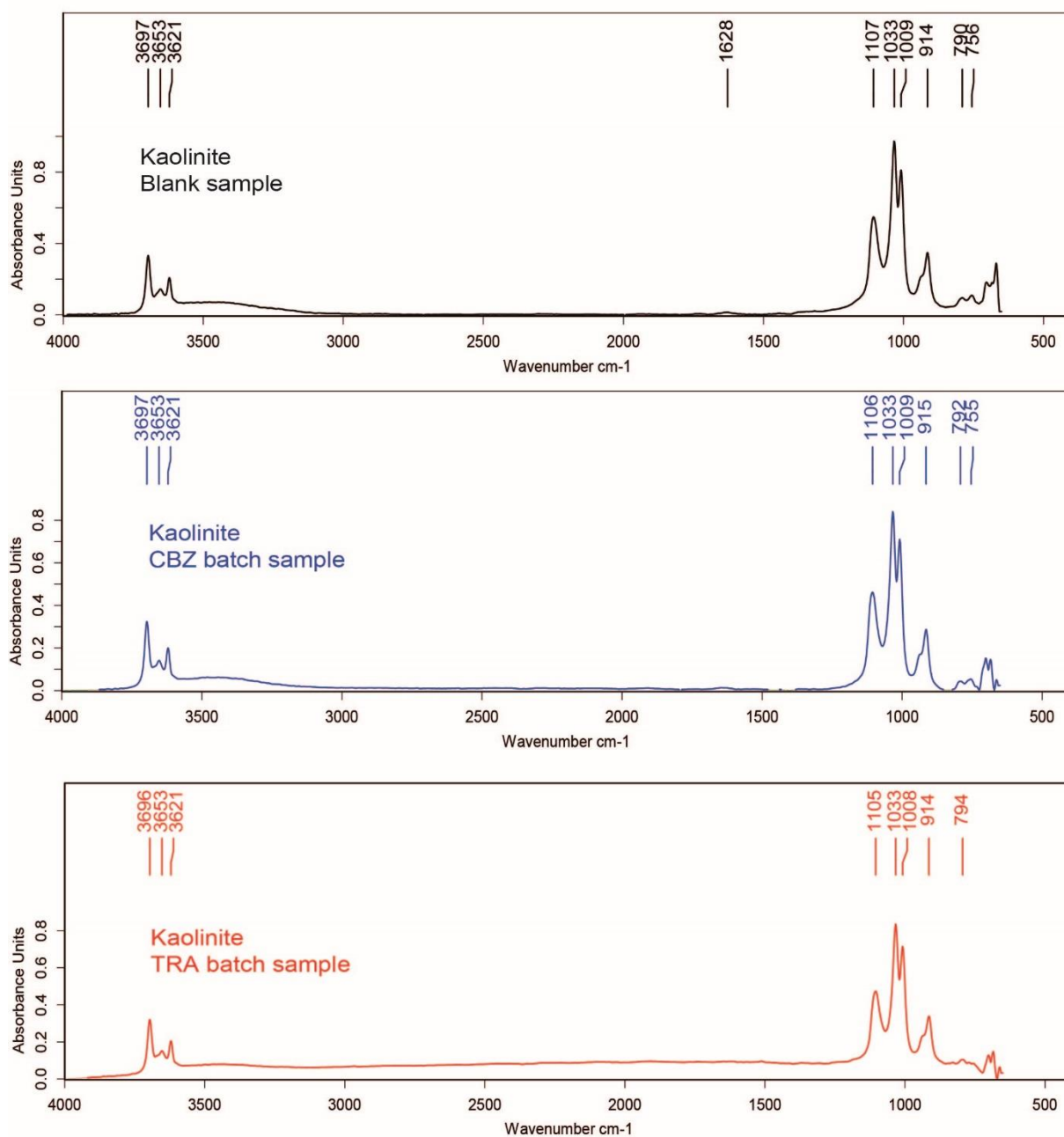


Figure 5. 4: FTIR spectra of kaolinite KGa2 samples: blank (in black), CBZ batch (in blue) and TRA batch (in red).

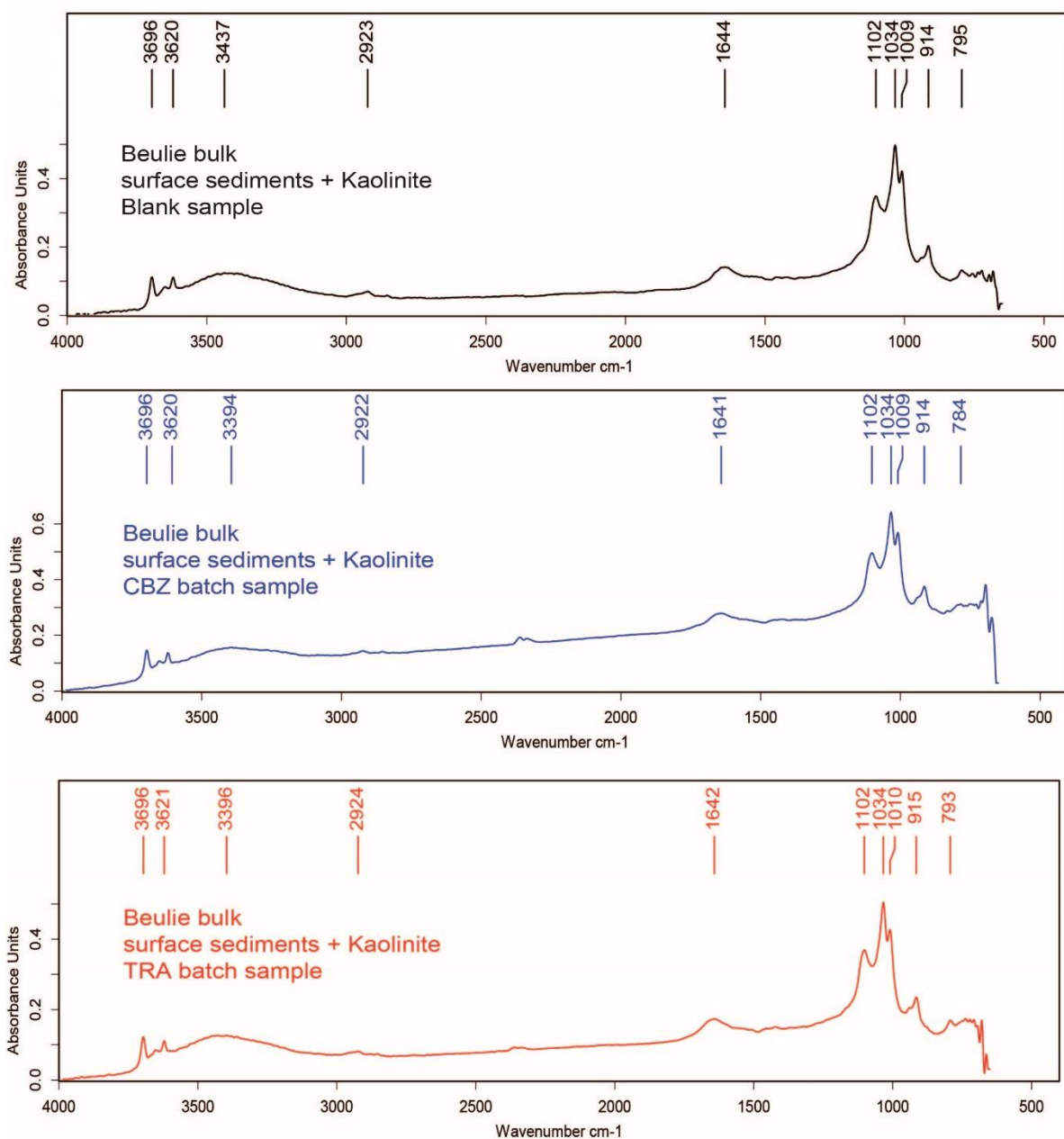


Figure 5. 5: FTIR spectra of Beulie pond surface sediments + kaolinite KGa2 samples: blank (in black), CBZ batch (in blue) and TRA batch (in red).

4. Discussion and perspectives

4.1. Sorption and desorption kinetics: a question of right of way?

The general sorption/desorption behaviour observed for CBZ, OXA, DIA and TRA (Figure 5.1) is consistent with their concentrations measured in the waters recovered after the wet-sieving procedures, highlighting a desorption of CBZ, OXA and DIA from sediment and an adsorption of TRA onto sediment (Chapter 4, Section 3.3.2). However, PAR exhibited results consistent with a sorption onto sediment, in opposition with results obtained after both wet-sieving procedures (Appendix 5, Table S5.1). Concerning DIC, two different trends appeared, with a first apparent adsorption onto sediment followed by an apparent desorption from sediment. CBZ, TRA and PAR sorption/desorption kinetics were fast, since a stabilization occurred after 10 minutes of stirring. However, other studies performed on PPs sorption/desorption kinetics run on hours or even days highlighted a first fast sorption/desorption followed by a much slower sorption/desorption (Kan et al., 2000; Chen et al., 2004). The 2-step kinetics observed for OXA, DIA and DIC within the hour of the experiment might be related to the liberation of ions into the dissolved phase, thus offering available sorption sites to PPs, as supported by the decrease in the electrical conductivity during the experiment (Table 5.1). This would suggest a competition between major species and PPs for sorption sites, as proposed by previous studies (Schmidtova et al., 2020; Grabic et al., 2022). Furthermore, this supports the major role played by the composition of sediment and of the overlying water in the sorption/desorption behaviour of PPs. Another parameter likely to influence the sorption/desorption hierarchy between PPs, and possibly explaining their respective kinetics, was the bonding strength. Indeed, charged molecules within the pH range measured during the experiment (Table 5.1), like TRA, are likely to form electrostatic interactions with sediments negatively charged edges, whereas neutral molecules will form either hydrogen bonds, hydrophobic interactions or π - π electron donor-acceptor interactions, thanks to their aromatic rings (Zhong et al., 2025), depending on the available sites.

There actually exist numerous factors susceptible to influence the sorption/desorption behaviour of PPs, such as the microbial growth (Hajj-Mohamad et al., 2017), particularly difficult to control and estimate experimentally. Recent studies therefore pointed the relevance of molecular simulations and geochemical calculations as complementary tools to laboratory experiment (Schaumann and Thiele-Bruhn, 2011; Ahmed et al., 2015), although

these approaches require a preliminary fine characterization of the carrying matrices, especially OM (Ahmed et al., 2012).

4.2. Carbamazepine and Tramadol sorption onto the particulate phase: a matrices team work?

Sorption experiments performed on Beulie pond surface sediments and/or kaolinite with CBZ or TRA solutions revealed the higher adsorbed concentration of both PPs onto the complex matrix (i.e., surface sediments) compared with a simple one (i.e., kaolinite KGa-2). During the preparation of batch samples, solid phases were mixed with a 0.01 M CaCl_2 solution before the addition of CBZ and TRA solutions prepared in the same 0.01 M CaCl_2 matrix. Indeed, the CaCl_2 solution was used in order to reach ionic conditions close to those occurring in pond water (Appendix 5). However, this implies an occupation of kaolinite sites by divalent Ca^{2+} cations, reducing the number of available sites for CBZ and TRA and thus reducing the adsorbed concentration of both PPs onto kaolinite. In addition, kaolinite contribution to surface sediments composition represents less than 10 wt% while total organic carbon contribution reaches almost 15 wt% (Humbrecht et al., 2025). This may underwrite the role played by other matrices part of surface sediments composition in the sorption of PPs, in particular OM. Furthermore, OM characteristics, for instance its composition in functional groups and the freshness of its coarser (i.e. >1 mm) grain-size fraction, support its availability to create bonds with PPs (*cf* Chapter 4). Moreover, TRA is constituted by 3 polar functional groups, which are an aromatic ether group, a tertiary alcohol group and a tertiary amine group, while CBZ is only constituted by an amide polar functional group (Knox et al., 2024). This suggests that TRA has a higher potential to form bonds with OM functional groups than CBZ.

The third solid phase used in batch experiments consisted in a combination of kaolinite (25 wt%) and of surface sediment (75 wt%). The theory exposed by McCarthy et al. (1981) regarding the sorption onto independent phases suggests that the sorption capacity of the global matrix is equal to the sum of the sorption capacity of each independent phase weighted by their mass contribution to the global matrix. In the case of the present batch experiment, the adsorbed concentrations in both CBZ and TRA were found to be lower onto kaolinite than onto surface sediments. According to the theory (McCarthy et al., 2018), the adsorbed concentrations in CBZ and TRA onto the mixed phases should be in between those measured for the two separated solid phases (surface sediments and kaolinite). Indeed, this result was observed in the case of TRA. However, in the case of CBZ, the mean adsorbed concentration

quantified for the mixed phases was similar to the one quantified when surface sediment is alone. The same observation has been made, also in the case of CBZ, by Wang et al. (2018) and was attributed to the formation of organo-mineral complexes, the latter exhibiting a higher adsorbed concentration of CBZ than separated matrices. However, this complex was constituted of kaolin and humic acid, while in our case, the use of surface sediments instead of “pure” OM fraction might reduce the organo-mineral complex formation potential, since surface sediments also include inorganic matrices. This might explain the relatively small difference in the mean adsorbed concentration of CBZ when using surface sediment alone and kaolinite blended with surface sediment.

An additional experiment therefore aimed to compare the adsorbed concentrations in PPs onto leonardite, a reference humic acid (1S104H, International humic substances society) and onto kaolinite KGa-2. It also intended to evaluate the adsorbed concentration in PPs onto a “composite” phase consisted in a blend of leonardite and kaolinite. This experiment didn’t take part of the present chapter because of quantification and experimental setup improvements needed. The procedure and the preliminary results are presented in Appendix 7.

Conclusions

This chapter has initiated the investigation of the sorption/desorption kinetics of 6 PPs, including CBZ, OXA, DIA, PAR, TRA and DIC. Relatively fast kinetics of either sorption or desorption were recorded in the case of CBZ, PAR and TRA. However, in the case of OXA, DIA and DIC, 2-step kinetics appeared within the hour of stirring, possibly explained by major elements exchanges between sediments and water, conducting to a competition for sediments binding sites. The sorption experiment performed with dry surface sediment and kaolinite KGa-2 as carrying phases, and with CBZ and TRA spiked solutions (10 mg/L and 20 mg/L, respectively) illustrated a higher adsorbed concentration in PPs onto sediment than onto kaolinite. Furthermore, in the case of CBZ, the adsorbed concentration measured in the case of mixed phases (surface sediment and kaolinite) raised the hypothesis of a synergy occurring between surface sediments matrices and kaolinite, as already supported by a previous study in the literature, highlighting the formation of organo-mineral complexes. However, the dilution of the organic fraction of surface sediments by other matrices such as quartz and the similarity of FTIR spectra performed on the solid phase with and without PPs prevented from confirming this hypothesis experimentally.

This preliminary investigation on PPs behaviour in the water-sediment continuum highlighted differences mainly explained by PPs charge and physico-chemical conditions occurring in the water-column, such as oxygenation. However, it confirmed the role played by surface sediments as complex matrices, and the need to not only consider potential carrying matrices separately, since the sorption capacity of surface sediment follows apparently no linear relationship with sediment individual matrix sorption capacities. As suggested by recent studies, geochemical calculation and molecular modelling could help deciphering and quantifying the different factors driving PPs sorption/desorption behaviour. However, these factors are not easy to determine experimentally, and thus a first characterization using analytical method is required.

Conclusions, limits and perspectives

1. Conclusions of the present study

The present study allowed to identify the main processes likely to describe the behaviour of PPs in the water-sediment continuum at the Beulie pond scale. The Beulie pond was found to be a retention area capable of accumulating a fraction of the particulate phase transferred at the Egoutier catchment scale, and thus PPs adsorbed onto the particulate phase. The spatial and statistical study performed at the pond scale highlighted a heterogeneous spatial distribution of the particulate phase. The granulometric characterization of surface sediments collected at the water/sediment interface of the Beulie pond coupled with classic sedimentation mechanisms revealed the preferential accumulation of the coarsest grain-size fraction (i.e. >1 mm) in the delta located at the inlet of the pond, while the finest grain-size fraction (i.e. <63 μm) was more concentrated in the main decantation basin, located close to the outlet. Moreover, the geochemical characterization of surface sediments indicated higher concentrations in total organic carbon (TOC) and more particularly in organic matter (OM) from terrestrial origin, and in PPs in general in the delta, and higher concentrations in OM from aqueous origin in the main decantation basin. Furthermore, the physico-chemical characterization of the water-column revealed heterogeneous oxygenation of the water/sediment interface at the pond scale. These last two points particularly supported the further investigation of OM characteristics in terms of typology and reactivity, the latter being appearing to be a potential carrying phase of PPs. Indeed, its diagenesis is likely to determine PPs fate in the water-sediment continuum, and might be driven by physico-chemical parameters, such as dissolved O_2 and redox potential, occurring at the water-sediment interface.

The following investigation of OM properties was performed on surface sediments collected in the pond's delta, particularly rich in OM. OM was therefore quantified and its typology and reactivity determined in 5 grain-size fractions of surface sediments, as well as contents in PPs. It appeared that the OM contained in the coarsest (>1 mm) grain-size fraction was different from the one contained in the finest (<63 μm) fraction, and exhibited particularly a higher TOC content, a better preservation, and a higher functionalization. Concerning PPs, their concentrations were found to be higher in the coarsest fraction than in the finest fraction. Nevertheless, the wet-sieving procedure employed to divide surface sediments into 5 grain-size fractions brought notably CBZ, OXA and DIA, three neutral PPs, to desorb from

the particulate phase, and TRA and VFX, two cationic PPs, to adsorb onto the particulate phase while they were initially belonging to the pond water used for the wet-sieving procedure. These results together highlighted the probable weaker bonds between OM and neutral PPs functional groups, and the probable stronger affinity of cationic PPs for OM. They also illustrated the influence of the oxygenation of water and the disturbance it might generate on the equilibrium initially occurring between sediments and water at the water-sediment interface. Since such an oxygenation of the water-column at the water-sediment interface has been observed during a previous sampling (Humbrecht et al., 2025), it raised the question of the stability of PPs trapping on the particulate phase in the natural environment.

The experimental kinetic approach revealed that the sorption/desorption kinetics of PPs were not instantaneous, with even an apparent hierarchy between molecules, attributable to PPs physico-chemical properties, the physico-chemical conditions of the experiment and also those occurring in the field, as well as the composition of the overlying water implying other dissolved species. Batch experiments including PPs solution and three different solid phases (bulk sediment only, kaolinite only or 75 wt% bulk sediment/25 wt% kaolinite) highlighted a better adsorbed concentration in PPs onto the “complex” (surface sediments) than onto the “pure” one (kaolinite), which provided information about the characteristics of sediment such as its composition in OM promoting the adsorption of PPs, as well as indices of a possible “team work” between sediment matrices, such as the formation of organo-mineral complexes, enhancing the sorption of PPs.

2. General conclusions

The coupled field-lab approach proposed in the present work demonstrated the relevance of a preliminary sampling with a high-spatial resolution, considering the spatial heterogeneity of the particulate phase accumulated within the Beulie pond. Furthermore, it allowed to identify preferential accumulation areas in terms of TOC and PPs contents. If the particulate phase, as a carrying matrix of PPs, has been part of many studies, the fine characterization of the particulate phase, and especially of its reactive matrices such as OM and clay minerals, was necessary to decipher the main drivers of PPs affinity for the particulate phase. The quantification of OM, completed with the determination of its typology, its origin, its functional groups and its reactive properties in the different grain-size fractions of surface sediments provided insights of the behaviour of PPs in the water/sediment continuum. Finally, the experimental approach, including kinetic and sorption batch experiments, completed the extensive analytical approach by providing information on both

the dynamics of PPs within the water-sediment continuum in terms of stability and reversibility, as well as the sorption capacity of surface sediments regarding both their composition in reactive matrices and the physico-chemical conditions occurring in the natural environment.

3. Limits of the present study

The present study still requires methodological improvements and developments, since a lack of information of the precise distribution and behaviour of PPs in the water/sediment continuum remains.

- The wet-sieving method employed to fraction surface sediments as a function of their grain-size revealed both sorption and desorption of PPs from surface sediments. Although this process allowed to make the link between the preservation and the reactivity of OM in these fractions and their respective contents in PPs, it prevented from calculating the mass-balance of PPs onto the particulate phase grain-size fractions.
- The kinetic experiment using water collected at the water/sediment interface integrated the complexity brought by pond water chemical composition. This made difficult the explanation of PPs behaviour during the experiment, since they are competing with each other's but also with the other dissolved species for sorption sites.
- Sorption batch experiment were performed using one complex matrix that is surface sediment and one simple matrix that is kaolinite. Results showed the higher adsorption of PPs onto surface sediments than onto kaolinite for both CBZ and TRA. However, the complexity of surface sediment still prevented from deciphering its intrinsic properties explaining this result compared with kaolinite. Although OM seemed to be a good candidate to carry PPs considering the main conclusions of Chapter 4, its precise contribution remains unclear. Furthermore, performing batches with individual reactive sediment matrices does not provide a complete picture, as it does not consider the synergy operating in the natural environment. Batches were set up with one concentration of either CBZ or TRA, which prevented from evaluating experimentally the competition between the two PPs, as well as the effect of an increasing initial concentration in both PPs on their adsorption onto solid phases.
- The water-sediment continuum also includes the colloidal fraction (3.5 kDa – 0.45 μ m), which was not investigated in this study, although this fraction has proven to play a

key role in PPs sorption and mobility. The isolation of the colloidal fraction from the water sediment continuum is still challenging. Therefore, an experimental approach using dissolved leonardite humic acid in dialysis bag was performed. This approach eventually highlighted the instability of complexes between ligand such as dissolved organic matter and PPs. Although these complexes are likely to occur in the natural environment, such processes remain hardly reproducible in laboratory.

- Chapter 2 presented data of concentrations in CBZ and TRA in the particulate phase upstream (suspended particulate matters), within (surface sediments) and downstream (suspended particulate matters) the Beulie pond. If it was clear that CBZ and TRA accumulated within the Beulie pond, they were still quantified downstream in suspended particulate matter, which shows that they are only partially trapped in the Beulie pond. Furthermore, Chapter 4 and 5 demonstrated the potential reversibility of the trapping of PPs onto surface sediments, especially under changes in oxygenation conditions. As these oxygenation conditions was found to vary along the year, the accuracy of the mass-balance of PPs adsorbed to the particulate phase is hardly reachable, and would require long-term physico-chemical measurements in the water-column and in the stream, completed with high-frequency samplings and water flow rate continuous measurements.

4. Perspectives

The present work presented new evidences of the role played by OM in the sorption of PPs onto the particulate phase, in terms of content but also in terms of composition, typology and reactive properties. It more particularly highlighted the fractions of OM exhibiting the highest affinity for PPs, in relation with the physico-chemical conditions in the water-column. This could lead to the development of experimental setups, including an extraction of the organic fractions of interest, the artificial creation of organo-mineral complexes using natural matrices from the field with the application of physico-chemical conditions similar to those measured in the natural environment, and sorption batch experiment in order to obtain sorption isotherms of PPs and sorption model parameters indicating the intensity of the sorption of PPs. Furthermore, organo-mineral interactions with PPs were also observed in other studies, such as the adsorption of PPs onto organoclays (De Oliveira et al., 2017; Guégan et al., 2020) and also involving the use of nanoparticles (NPs) in an *in-situ* experiment and investigating NPs-OM complex synergy and reactivity on the removal of PPs in the Egoutier contaminated watershed (Veselská et al., 2025). Such study

both provides insights on the behaviour of such complexes in the natural environment and offers potential remediation solutions to limit PPs diffusion in the environment.

This work also allowed to identify the Beulie pond as a hotspot of PPs sorbed onto surface sediments. Furthermore, it highlighted the delta of the pond as the principal local hotspot at the pond scale, characterized by high concentrations in PPs, but also in organic matter from terrestrial origin. These results support the efficiency of retention areas in general to limit the diffusion of PPs in the environment, although the trapping remains partial. Moreover, the results of the Chapter 4 indicated specific fractions of organic matter likely to create bonds with PPs, considering the physical-chemical properties of the water-column. This suggest that an operational perspective of PPs trapping in the natural environment could be found in artificial retention areas, already used in this purpose, with controlled conditions in terms of organic matter inputs and physical-chemical properties of the overlying water, likely to limit the reversibility of PPs sorption onto the particulate phase.

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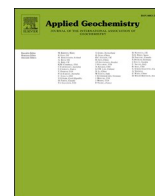
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Appendix 1: Effect of sediment composition and accumulation on pharmaceutical product spatial distributions at the suburban pond scale (Beulie pond, SNO Observil, France), edited version



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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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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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 ($<63 \mu\text{m}$).

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

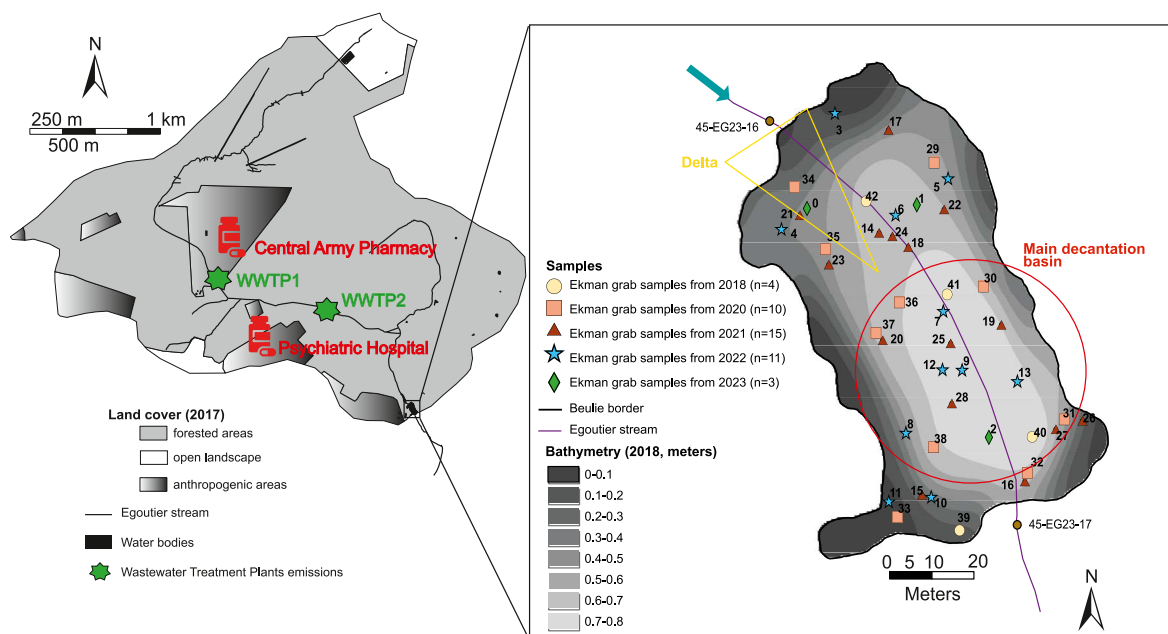


Fig. 1. Map representing the Beulie pond catchment area with information about soil occupation collected from Corine Land Cover data from 2017. The Egoutier stream is represented by the black continuous line. The two wastewater treatment plants connected to 1- the central army pharmacy and 2- a psychiatric 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 ($HI = (S2 \times 100) / TOC$ expressed in $mgHC.g^{-1}TOC$, 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 ($<2\text{ }\mu\text{m}$), fine silt ($2\text{--}20\text{ }\mu\text{m}$), coarse silt ($20\text{--}63\text{ }\mu\text{m}$), fine sand ($63\text{--}250\text{ }\mu\text{m}$) and coarse sand ($250\text{--}1800\text{ }\mu\text{m}$) 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 $\leq 63\text{ }\mu\text{m}$), was particularly investigated in this study to track the silty to clay fraction. The samples were dried at $45\text{ }^{\circ}\text{C}$, 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, Nederland) operating in parafocussing Bragg-Brentano geometry. The diffractometer was equipped with iron-filtered $Co\text{ K}\alpha$ 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 $45\text{ }^{\circ}\text{C}$, 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 (logK_{ow}).

	pKa	Principal charge state at Beulie pond pH	Persistence in the aquatic environment	logK _{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 ^e	Neutral	Moderate ^k	2.70 ^f
Paracetamol	9.5 ^e	Neutral	Low ^j	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

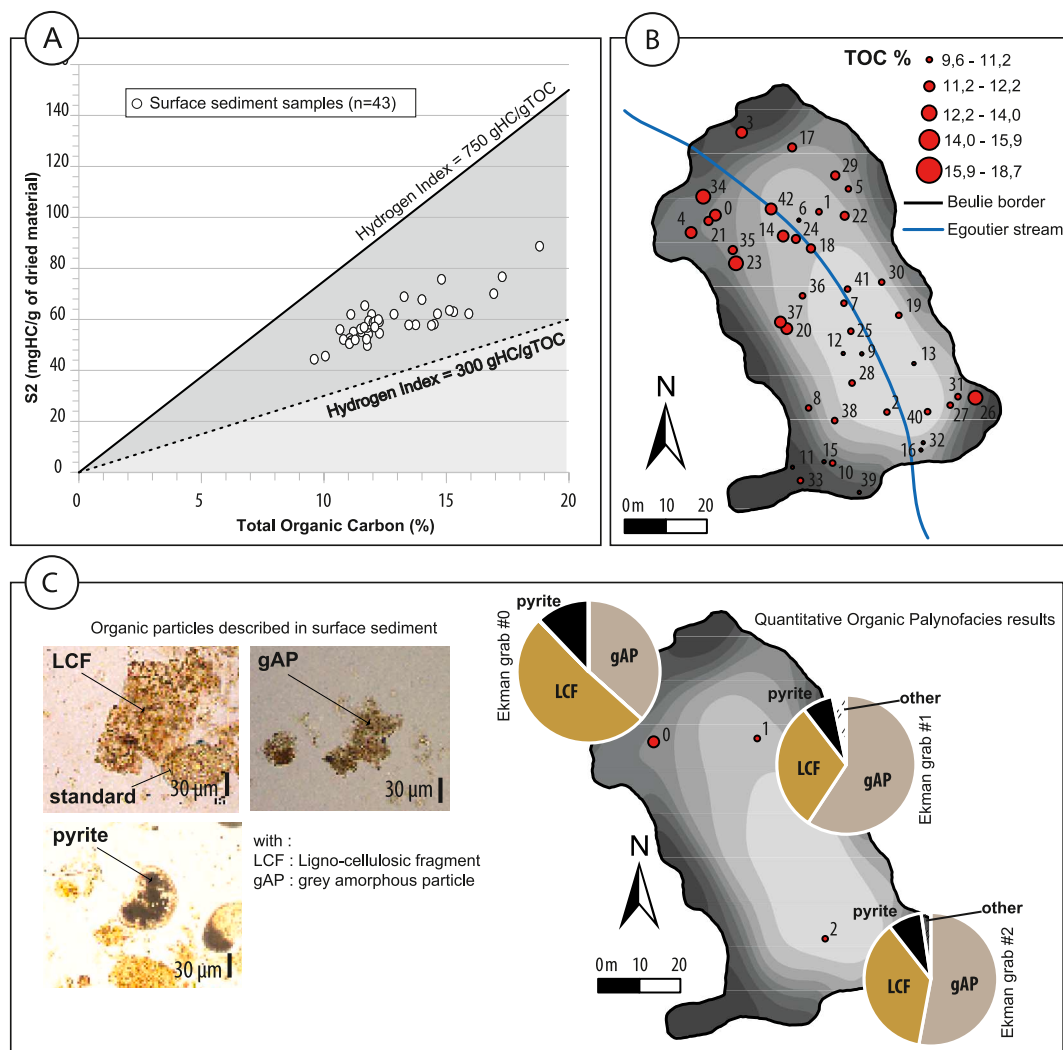


Fig. 2. S2 peak (mgHC/g of dried material) as a function of Total Organic Carbon (TOC, %), calculated for 43 surface sediments collected between September 2018 and September 2023 (A). Map representing the spatial distribution of TOC contents of sediment samples at the Beulie pond scale (B). Palynofacies 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

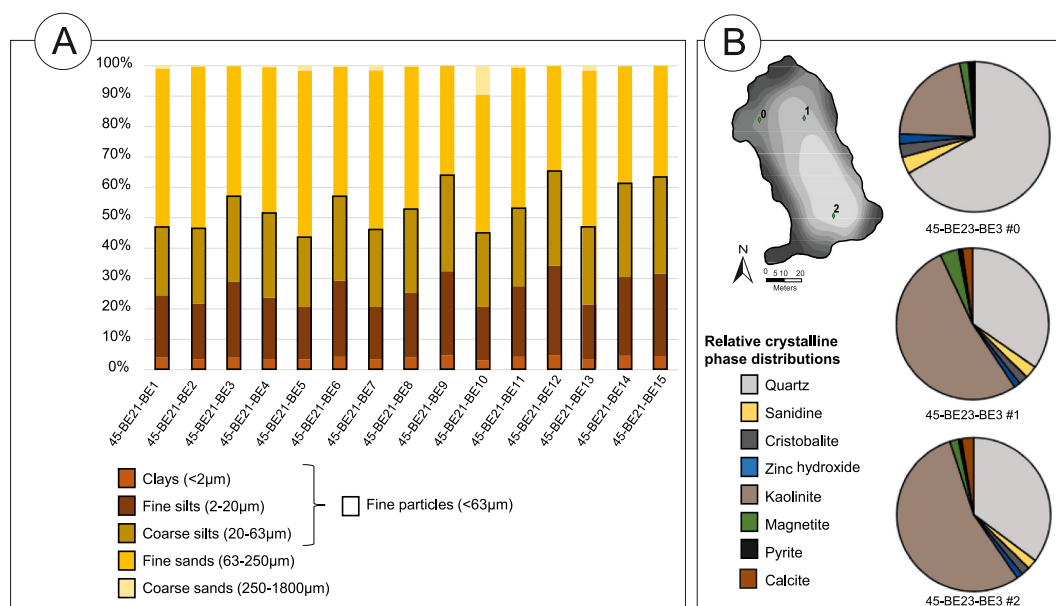


Fig. 3. Granulometric distribution given in % for the 15 samples collected in September 2021. (A). Relative crystalline phase distribution for the 3 bulk sediment samples collected in September 2023, including the composition in Quartz, Sanidine, Cristobalite, Zinc hydroxide, Kaolinite, Magnetite, Pyrite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

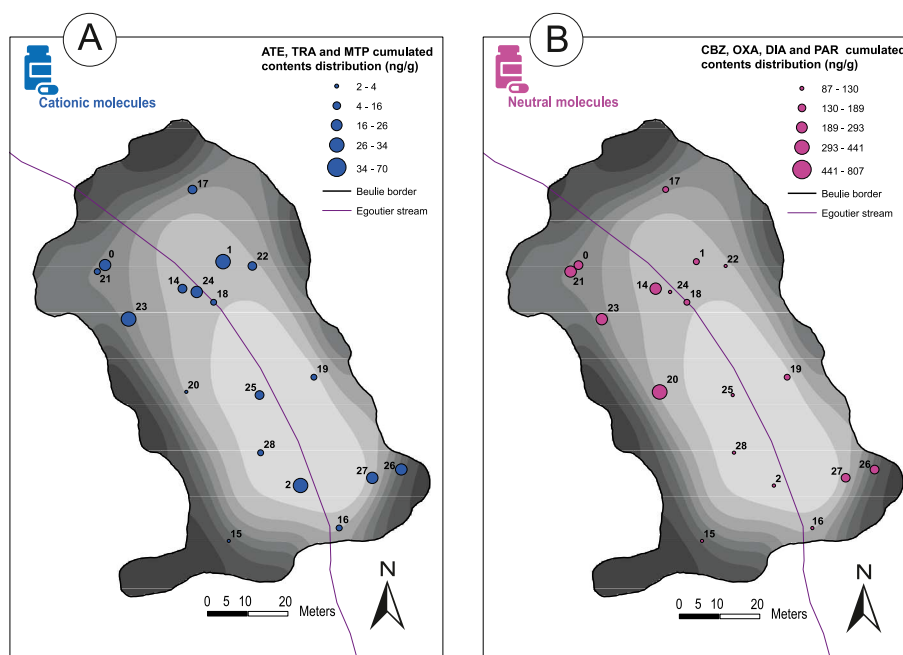


Fig. 4. Spatial distribution at pond scale of cumulated contents in cationic pharmaceutical products, including ATE, TRA and MTP (A). Spatial distribution at pond scale of cumulated concentration in neutral pharmaceutical products, including CBZ, OXA, DIA and PAR (B). Contents were quantified in 15 samples 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 heterogeneous spatial distribution at the pond scale, with a preferential accumulation in the delta, as well as differences in its palynofacies composition, depending on surface

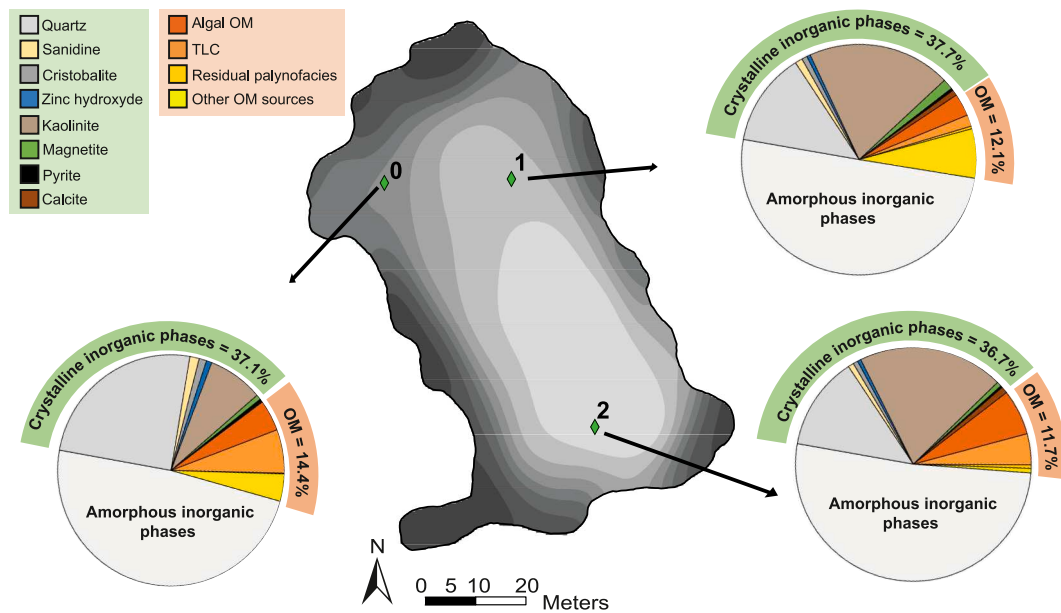


Fig. 5. Crystalline and organic compositions of surface sediment samples collected in September 2023 within the Beulie pond.

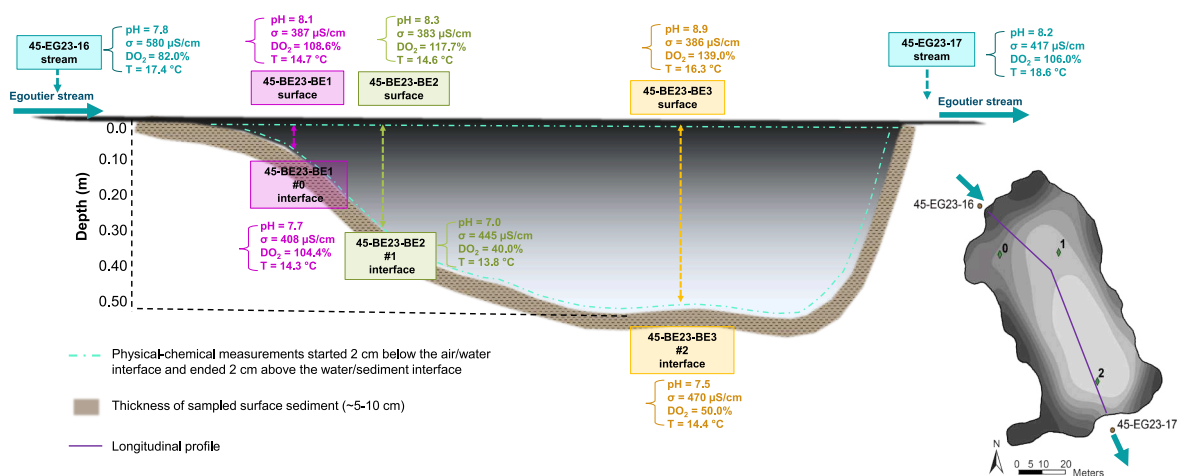


Fig. 6. Longitudinal profile performed from the delta to the main decantation basin of the Beulie pond. Physical-chemical measurement, including pH, electrical conductivity (σ), dissolved O_2 (DO_2) and temperature (T), were conducted in the stream at the pond's inlet (45-EG23-16), in the delta (45-BE23-BE1),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

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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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Supplementary Materials

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

Number of Tables: 7

Number of Figures: 3

Number of Text: 1

Table S2. 1 (cited as Table S1 in the edited article): Rock-Eval parameters including S2 peak (mgHC/gDS=dried sediment) and Total Organic Carbon (TOC, %), calculated for 43 sediment samples collected within the Beulie pond between September 2018 and September 2023.

Sets	Sample names	Sample ID	Longitude (°)	Latitude (°)	TOC (%)	S2 peak (mgC/gDS)
2023	45-BE23-BE1	0	1.95770	47.9422596	14.4	58.2
	45-BE23-BE2	1	1.95818	47.942225	12.1	59.0
	45-BE23-BE3	2	1.95832	47.941913	11.7	55.9
2022	45-BE22-BE1	3	1.95783	47.94246	15.9	62.3
	45-BE22-BE4	4	1.95767	47.94224	14.6	62.3
	45-BE22-BE7	5	1.95818	47.94234	11.5	55.2
	45-BE22-BE9	6	1.95802	47.94227	11.2	55.1
	45-BE22-BE12	7	1.95817	47.94209	11.8	54.3
	45-BE22-BE13	8	1.95806	47.94186	11.7	49.8
	45-BE22-BE14	9	1.95823	47.94198	11.0	52.6
	45-BE22-BE19	10	1.95814	47.94174	11.7	52.3
	45-BE22-BE20	11	1.95801	47.94173	11.1	51.7
	45-BE22-BE23	12	1.95817	47.94198	10.8	52.1
	45-BE22-BE24	13	1.9584	47.94196	11.0	50.7
2021	45-BE21-BE1	14	1.95797	47.942235	15.2	63.1
	45-BE21-BE2	15	1.958112	47.941743	11.0	50.5
	45-BE21-BE3	16	1.958427	47.941771	10.0	45.6
	45-BE21-BE4	17	1.957995	47.942429	12.8	62.2
	45-BE21-BE5	18	1.95806	47.942209	13.7	57.9
	45-BE21-BE6	19	1.958349	47.942065	11.2	52.0
	45-BE21-BE7	20	1.957985	47.942033	15.1	63.6
	45-BE21-BE8	21	1.957726	47.942266	13.4	57.9
	45-BE21-BE9	22	1.958169	47.942281	12.2	59.1
	45-BE21-BE10	23	1.957817	47.942174	17.2	76.9
	45-BE21-BE11	24	1.958011	47.942229	12.2	54.6
	45-BE21-BE12	25	1.958194	47.942029	12.0	58.2
	45-BE21-BE13	26	1.958602	47.941887	16.9	70.2
	45-BE21-BE14	27	1.95852	47.94187	11.8	56.9
	45-BE21-BE15	28	1.9582	47.941916	11.8	58.2
2020	45-BE20-BE1	29	1.958136	47.942369	13.2	69.0
	45-BE20-BE2	30	1.958292	47.942137	11.8	59.5
	45-BE20-BE3	31	1.958545	47.941889	12.0	58.9
	45-BE20-BE4	32	1.958434	47.941787	10.6	56.1
	45-BE20-BE5	33	1.958036	47.941701	12.0	59.2
	45-BE20-BE6	34	1.957708	47.942319	18.7	89.0
	45-BE20-BE7	35	1.957806	47.942203	14.0	67.9
	45-BE20-BE8	36	1.958035	47.942105	12.2	60.0
	45-BE20-BE9	37	1.957964	47.942047	14.7	75.9
	45-BE20-BE10	38	1.958145	47.941833	11.5	56.3
2018	45-BE18-BE2	39	1.958228	47.941677	9.6	44.4
	45-BE18-BE3	40	1.958447	47.941855	11.6	57.0
	45-BE18-BE4	41	1.958181	47.942121	12.0	57.1
	45-BE18-BE5	42	1.957929	47.942294	14.3	57.8
Maximal value					18.7	89
Minimal value					9.6	44.4
Mean value					12.7	58.8
Standard deviation					2.0	8.2

Table S2. 2 (cited as Table S2 in the edited article): Granulometric fraction distributions, given in %, and calculated for the 15 surface sediments collected in September 2021. Fine particles composition designates cumulated compositions in clays, fine silts and coarse silts. The measurements have been performed in duplicates, and the presented values correspond to the average of the two replicates.

Sample names	Sample ID	Clays (<2 μm)	Fine silts (2-20 μm)	Coarse silts (20-63 μm)	Fine sands (63-250 μm)	Coarse sands (250-1800 μm)	Fine particles (<63 μm)
45-BE21-BE1	14	4.0	20.5	22.4	52.2	0.9	46.9
45-BE21-BE2	15	3.5	18.2	25.0	53.1	0.2	46.7
45-BE21-BE3	16	4.0	25.1	28.3	42.5	0.1	57.4
45-BE21-BE4	17	3.5	20.2	27.9	47.9	0.4	51.6
45-BE21-BE5	18	3.4	17.2	23.3	54.4	1.7	43.9
45-BE21-BE6	19	4.3	25.1	27.9	42.4	0.3	57.3
45-BE21-BE7	20	3.5	17.4	25.2	52.4	1.5	46.1
45-BE21-BE8	21	4.1	21.1	27.4	47.1	0.2	52.7
45-BE21-BE9	22	4.7	27.7	31.7	35.8	0.0	64.1
45-BE21-BE10	23	3.1	17.4	24.1	45.4	9.5	44.7
45-BE21-BE11	24	4.3	23.2	25.8	46.1	0.6	53.3
45-BE21-BE12	25	4.7	29.6	31.0	34.7	0.1	65.2
45-BE21-BE13	26	3.3	18.2	25.9	50.9	1.6	47.4
45-BE21-BE14	27	4.6	25.9	31.2	38.2	0.1	61.7
45-BE21-BE15	28	4.5	27.0	31.9	36.5	0.0	63.5
Maximal value		4.7	29.6	31.9	54.4	9.5	65.2
Minimal value		3.1	17.2	22.4	34.7	0.0	43.9
Mean value		4.0	22.3	27.3	45.3	1.2	53.5
Standard deviation		0.5	4.2	3.1	6.7	2.4	7.6

Text S2.1

Identified crystalline phases in the all three patterns of bulk materials are: SiO_2 (quartz, PDF card No. 01-078-1253), KAlSi_3O_8 (sanidine, PDF card No. 01-089-2650), SiO_2 (cristobalite, PDF card No. 04-005-4875), $\text{Zn}(\text{OH})_2$ (PDF card No. 04-012-2300), $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (kaolinite, PDF card No. 01-086-8542), Fe_3O_4 (magnetite, PDF card No. 01-078-3148), FeS_2 (Pyrite, PDF card no. 04-003-1989). Additionally, CaCO_3 (Calcite, PDF card No. 01-086-4272) occurred in the samples in the 45-BE21-BE2 #1 and 45-BE21-BE3 #2.

Table S2. 3 (cited as Table S3 in the edited article): Calculation of amorphous and crystalline phases content using internal standard method in 3 surface sediments (bulk samples without any treatment) collected in September 2023.

Sample names	Sample ID	Amorphous content (%)	Crystalline phases (%)
45-BE21-BE1 #0	0	62.9	37.1
45-BE21-BE2 #1	1	62.3	37.7
45-BE21-BE3 #2	2	63.3	36.7

Table S2. 4: (cited as Table S4 in the edited article): Quantification of crystalline phases in 3 surface sediments (bulk samples without any treatment) collected in September 2023 calculated using Rietveld refinement.

Sample names	Sample ID	Quartz (%)	Sanidine (%)	Cristobalite (%)	Zinc hydroxide (%)	Kaolinite (%)	Magnetite (%)	Pyrite (%)	Calcite (%)
45-BE21-BE1 #0	0	67.0	3.6	2.9	2.1	21.2	1.9	1.3	--
45-BE21-BE2 #1	1	34.7	2.7	2.0	1.3	52.4	3.9	0.9	2.1
45-BE21-BE3 #2	2	35.2	2.1	1.8	1.3	54.6	1.8	0.7	2.5

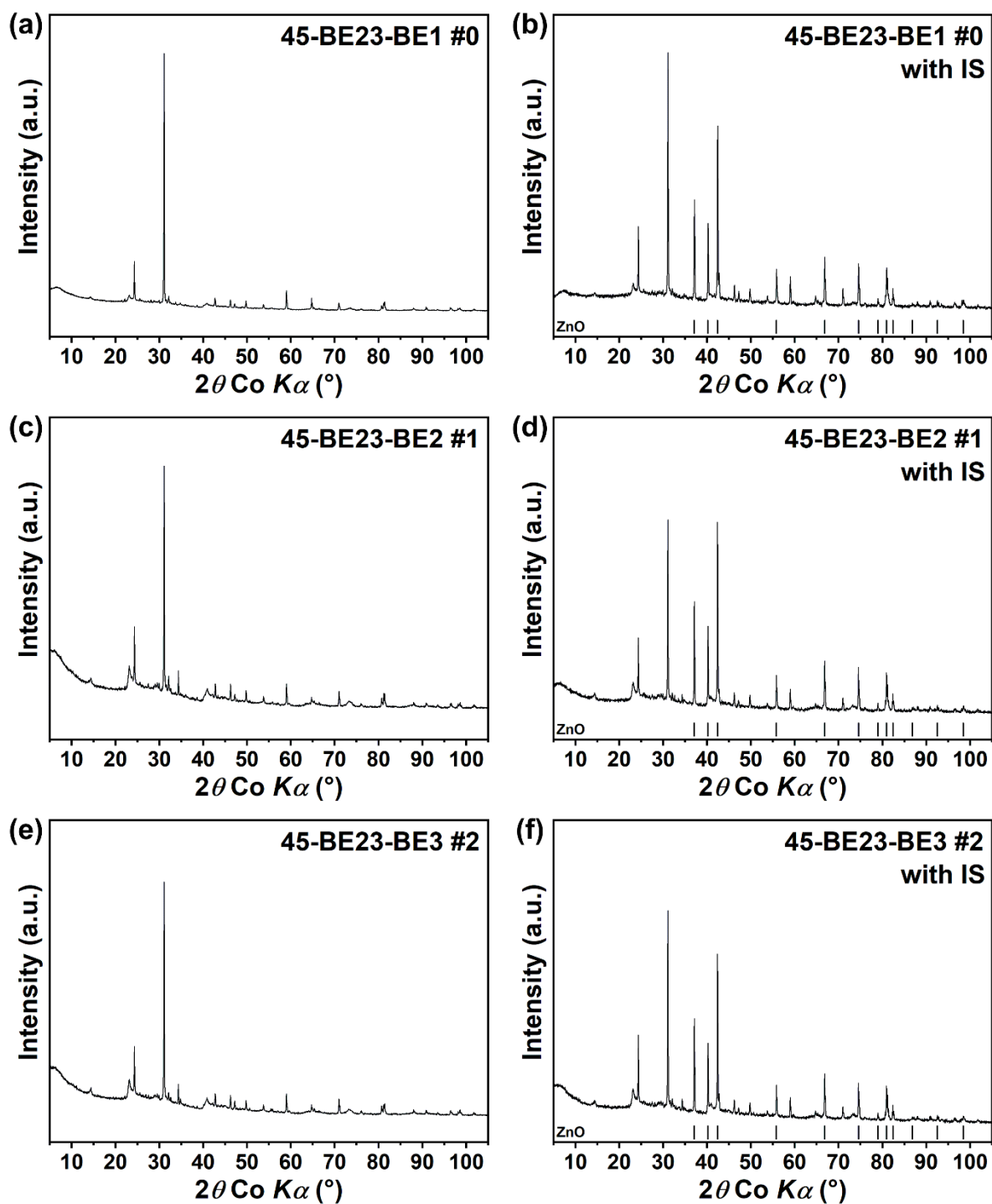


Figure S2. 1: (cited as Figure S1 in the edited article): XRD diffraction patterns of original bulk materials for crystalline phase identification and quantification (a, c, e), and with added internal standard (ZnO) used for calculation of amorphous content (b, d, f), IS=internal standard.

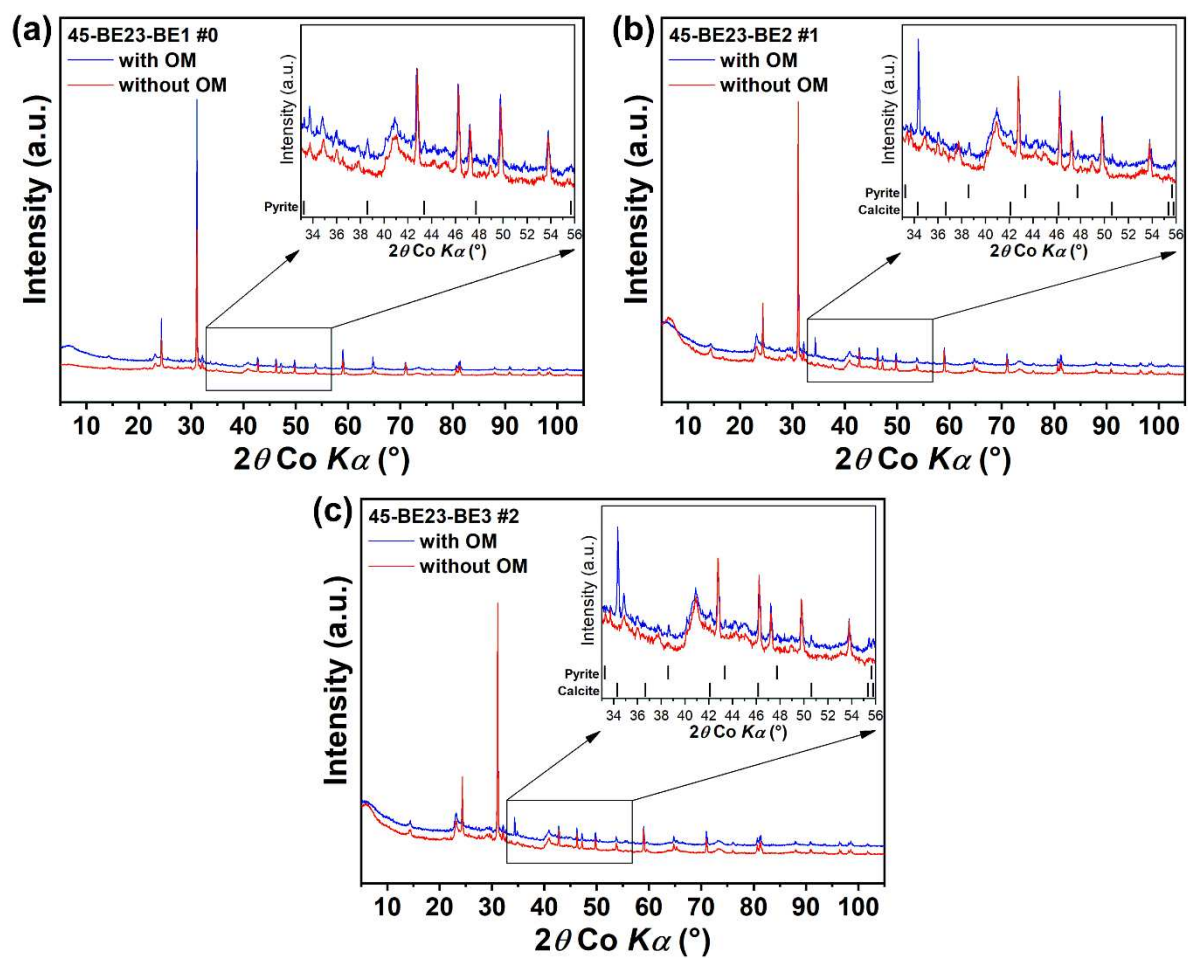


Figure S2. 2 (cited as Figure S2 in the edited article): Comparison of XRD patterns of bulk sediment with OM and with removed OM in the samples 45-BE23-BE1 #0 (a), 45-BE23-BE2 #1 (b), and 45-BE23-BE3 #2 (c) from September 2023.

Table S2. 5: (cited as Table S5 in the edited article): Pharmaceutical products (PP) content for: Tramadol (TRA), Atenolol (ATE), Metoprolol (MTP), Carbamazepine (CBZ), Diazepam (DIA), Oxazepam (OXA), and Paracetamol (PAR) measured in the 15 surface sediments collected within the Beulie pond in September 2021 and in the 3 surface sediments collected in September 2023. LOQ=Limit of quantification; LOD=Limit of detection.

Sets	Sample Names	Sample IDs	Cationic molecules contents (ng/g of dried sediment)				Neutral molecules content (ng/g of dried sediment)				
			ATE	TRA	MTP	Total	CBZ	OXA	DIA	PAR	Total
2021	45-BE21-BE1	14	2.8	6.3	14.0	23.2	101.6	281.3	56.0	1.9	440.8
	45-BE21-BE2	15	0.4	3.0	1.1	4.5	49.4	14.6	21.6	1.8	87.5
	45-BE21-BE3	16	4.9	4.1	1.2	10.2	58.5	44.4	25.2	1.0	129.2
	45-BE21-BE4	17	6.5	11.4	8.1	26.0	51.5	119.9	16.4	1.3	189.1
	45-BE21-BE5	18	1.2	5.6	4.7	11.6	86.7	79.0	1.9	1.2	168.8
	45-BE21-BE6	19	<LOD	11.1	1.4	12.5	68.3	15.7	103.9	1.0	188.9
	45-BE21-BE7	20	<LOD	1.4	1.1	2.5	109.6	316.2	377.9	2.6	806.2
	45-BE21-BE8	21	1.4	12.6	2.2	16.1	70.1	265.0	52.2	2.7	390.0
	45-BE21-BE9	22	4.1	4.7	11.3	20.2	56.9	63.2	8.8	1.5	130.4
	45-BE21-BE10	23	8.3	30.6	9.1	48.0	100.3	186.4	78.9	1.5	367.0
	45-BE21-BE11	24	9.1	9.0	12.7	30.8	80.0	5.8	38.9	1.3	126.0
	45-BE21-BE12	25	5.4	4.0	10.7	20.1	52.8	53.8	17.5	0.9	125.0
	45-BE21-BE13	26	2.7	12.7	15.8	31.1	75.8	157.5	17.4	2.0	252.8
	45-BE21-BE14	27	4.3	21.8	8.5	34.6	53.9	137.1	99.2	2.7	292.9
	45-BE21-BE15	28	<LOD	11.6	4.7	16.3	59.7	26.9	13.7	1.4	101.7
2023	45-BE23-BE1	0	<LOD	8.3	19.5	27.8	85.2	119.9	66.2	1.0	272.2
	45-BE23-BE2	1	<LOD	27.0	42.5	69.5	54.6	53.9	43.5	1.2	153.1
	45-BE23-BE3	2	<LOD	31.7	21.2	52.9	40.4	44.6	29.3	1.7	116.0
Maximal value			9.1	31.7	42.5	69.5	109.6	316.2	377.9	2.7	806.2
Minimal value			<LOD	1.4	1.1	2.5	40.4	5.8	1.9	0.9	87.5
Mean value			3.4	12.0	10.5	25.4	69.7	110.3	59.4	1.6	241.0
Standard deviation			3.0	9.5	10.2	17.4	20.3	96.6	85.1	0.6	176.5

Table S2. 6 (cited as Table S6 in the edited article): Analytical optimized conditions of PPs, with Retention Time (RT), Isotopically Labelled Internal Standards (ILIS) TRA for Tramadol, CBZ for Carbamazepine, OXA for Oxazepam and PAR for paracetamol, Multiple Reaction Monitoring (MRM) features for targeted PPs, Fragmentor (Frag.), Collision energy (Ce), Rec. the recovery ratio of the whole method in % estimated in spiked sediments (100 ng.g⁻¹) and limits of detection (LOD) and quantification (LOQ).

PPs	ILIS*	RT min	[M-H]	MRM 1	Ce eV	Frag V	MRM 2	Ce V	Rec. %	LOD ng g ⁻¹	LOQ ng g ⁻¹
Atenolol	TRA- ¹³ C ₃ D ₃	2.4	267.3	145.3	26	110	74.1	50	43 ± 8	0.4	1.3
Tramadol	TRA- ¹³ C ₃ D ₃	3.7	264.4	58.2	18	110	42.2	65	105 ± 4	0.2	0.7
Metoprolol	TRA- ¹³ C ₃ D ₃	3.6	268.4	116.1	14	110	77.1	65	62 ± 3	0.2	0.5
Carbamazepine	CBZ- ¹³ C ₆	5.1	237.3	194.1	18	110	165.1	50	102 ± 5	0.3	0.8
Oxazepam	OXA-D ₅	5.3	287.7	242.1	17	100	270.1	9	92 ± 9	0.4	1.3
Diazepam	OXA-D ₅	6.3	285.7	194.2	29	130	223.3	21	104 ± 5	0.3	0.9
Paracetamol	PAR-D ₄	2.0	152.2	110.1	10	110	65.1	30	97 ± 5	0.2	0.6

Table S2. 7 (cited as Table S7 in the edited article): pH, electrical conductivity, dissolved O₂ and temperature measured in the water-column in September 2023.

Sample names	Water-column depth (cm)	pH (pH units)	Electrical conductivity (µS/cm)	Dissolved O ₂ (%)	Temperature (°C)
45-BE23-BE1 #0	0	8.1	387	108.6	14.7
	5	8.1	401	107.4	14.6
	10	7.7	408	104.4	14.3
45-BE23-BE2 #1	0	8.3	383	117.7	14.6
	5	8.5	384	120.8	14.3
	10	8.6	385	121.3	14.2
	15	8.7	386	122.4	13.8
	20	8.6	386	122.5	13.7
	29	7.0	445	40.0	13.8
45-BE23-BE3 #3	0	8.9	386	139.0	16.3
	5	8.9	379	142.0	16.3
	10	8.9	381	138.0	15.0
	15	8.9	381	135.0	14.9
	20	8.8	383	133.0	14.6
	30	8.8	385	127.0	14.0
	40	8.7	387	121.0	14.0
	48	7.5	470	50.0	14.4

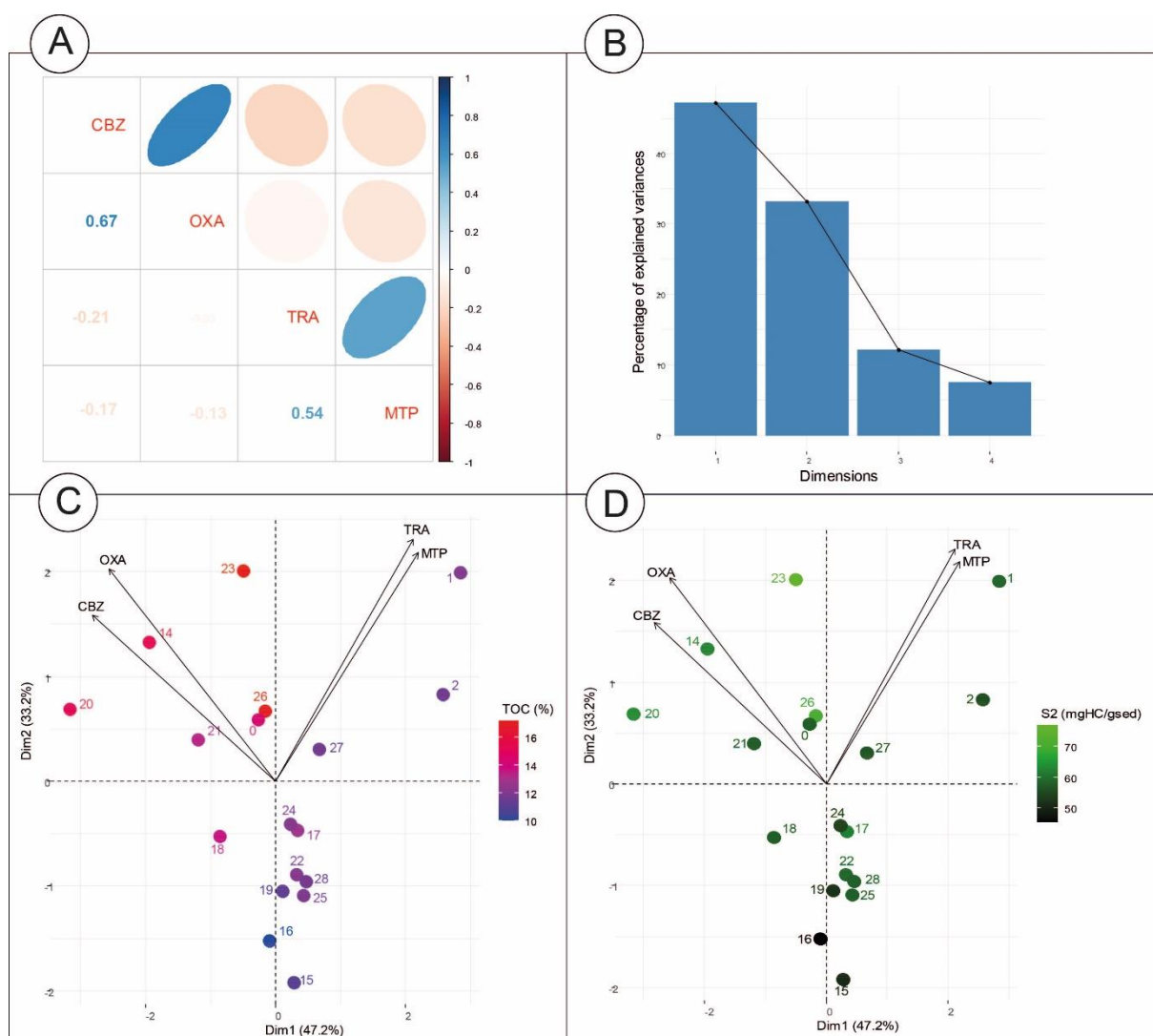


Figure S2. 3 (cited as Table S3 in the edited article): Principal Component Analysis (PCA) evaluating the spatial dispersion of pharmaceutical products contents at the pond scale, including CBZ, OXA, TRA and MTP contents. The correlation matrix (A), the eigenvalues (B), and the PCA biplots with a color scale regarding either the TOC content (C) or the S2 (D) are represented.

Appendix 3: Organic carbon and pharmaceutical products content grain-size distributions in surface sediment and in the water collected after a wet-sieving procedure (Beulie pond sampling from September 2023)

In order to determine the grain-size distribution of TOC and PPs within surface sediments (Chapter 4), a first wet-sieving procedure has been tested on surface sediments collected in three different areas of the Beulie pond: the delta (Z1), the upstream area (Z2) and the main decantation basin (Z3) (cf Chapter 3). This wet-sieving procedure was performed using ultra-pure water, in order to fraction surface sediments into 5 grain-sizes: >1 mm, 250 μ m-1 mm, 160 μ m-250 μ m, 63 μ m-160 μ m and <63 μ m. Surface sediment samples were collected in September 2023 in HDPE 250 mL bottles, at the water/sediment interface in the three areas. One bottle of wet surface sediments of each area was sieved using ultra-pure water, dried at 45 °C overnight and finely crushed in an agate mortar. One bottle of sediment from each sampled area was also directly dried at 45 °C overnight, corresponding to the bulk fraction. The particulate phase, including the 5 dried and crushed grain-size and bulk fractions, were analysed in order to quantify notably the total organic carbon (TOC) and pharmaceutical products (PPs) contents (only in the <63 μ m and bulk fractions in the case of PPs). The water at the water/sediment interface of each area was also collected, as well as the water recovered by centrifugation of the <63 μ m grain-size fraction at the end of the wet-sieving procedure. Both were filtered at 0.45 μ m prior to dissolved organic carbon (DOC) concentration and PPs dissolved concentration quantifications (Figure S3.1).

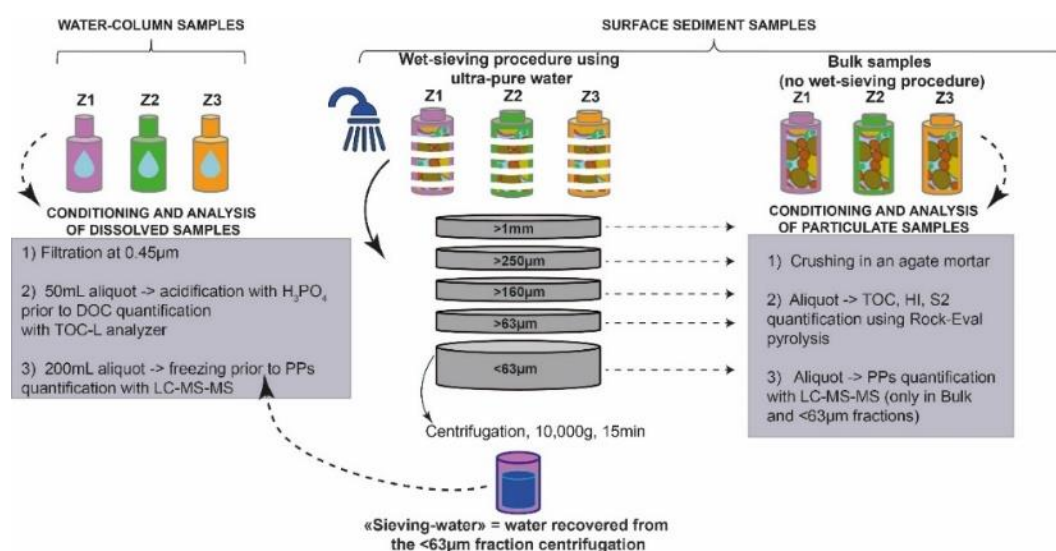


Figure S3. 1: Wet-sieving procedure using ultra-pure water, and water and surface sediment samples characterization including quantification of total organic carbon (TOC, %), S2 peak (mgHC/g dry sediment), hydrogen index (HI, mgHC/gTOC), dissolved organic carbon concentration (DOC, mg/L) and pharmaceutical products dissolved and particulate concentration (PPs, ng/L and ng/g respectively). Z1 = delta, Z2 = upstream area, Z3 = main decantation basin.

Table S3. 1: Rock-Eval parameters including S2 peak (mgHC/g dried sediment) and Total Organic Carbon (TOC, %), calculated for 3 sediment samples collected within the Beulie pond in September 2023, and for 5 grain-size fractions obtained after sediment samples wet-sieving procedure using ultra-pure water. Z1, Z2 and Z3 collected in the delta, in the upstream area and in the main decantation basin, respectively.

	Total dry mass (mg)	S2 (mgHC/g dried sediment)	TOC (%)	TOC (mg)	HI (mgHC/gTOC)
Z1 Bulk R1	31,100	66	14.6	4541	453
Z1 Bulk R2		65	10.2	3185	632
Z1 Bulk R3		66	10.0	3119	655
Z1 > 1mm		133	24.1	699	552
250 µm < Z1 < 1 mm	1198	153	27.6	331	553
160 µm < Z1 < 250 µm	74	210	39.6	29	530
63 µm < Z1 < 160 µm	1203	131	27.5	331	478
Z1 < 63 µm R1	22,383	53	12.1	2717	138
Z1 < 63 µm R2		53	12.1	2717	136
Z1 < 63 µm R3		53	12.2	2672	136
Z2 Bulk R1	30,500	62	12.0	3700	512
Z2 Bulk R2		61	9.0	2731	685
Z2 Bulk R3		63	12.1	3694	518
Z2 > 1 mm		147	21.0	68	700
250 µm < Z2 < 1 mm	165	149	22.4	37	668
160 µm < Z2 < 250 µm	74	154	32.0	24	481
63 µm < Z2 < 160 µm	853	108	21.4	183	505
Z2 < 63 µm R1	26,862	57	11.3	3029	507
Z2 < 63 µm R2		58	11.3	3026	511
Z2 < 63 µm R3		63	12.1	3253	518
Z3 Bulk R1	31,900	62	11.9	3807	523
Z3 Bulk R2		62	11.9	3791	519
Z3 Bulk R3		62	11.9	3799	520
Z3 > 1 mm		152	21.2	52	719
250 µm < Z3 < 1 mm	236	123	17.2	41	711
160 µm < Z3 < 250 µm	119	113	23.9	28	475
63 µm < Z3 < 160 µm	1126	70	14.2	160	494
Z3 < 63 µm R1	25,907	57	11.1	2877	511
Z3 < 63 µm R2		57	11.1	2884	516
Z3 < 63 µm R3		58	11.2	2892	518

The grain-size distribution of TOC content in the 3 surface sediments illustrated a major contribution of the finer (i.e. <63 µm) grain-size fraction, whatever the sampled pond's area. However, in the case of delta surface sediments (Z1), a sustainable contribution of the >1 mm grain-size fraction in the total mass of TOC (in mg) was observed. Indeed, the mass of this grain-size fraction in the delta is one order of magnitude higher than in the two other areas (Figure S3.2).

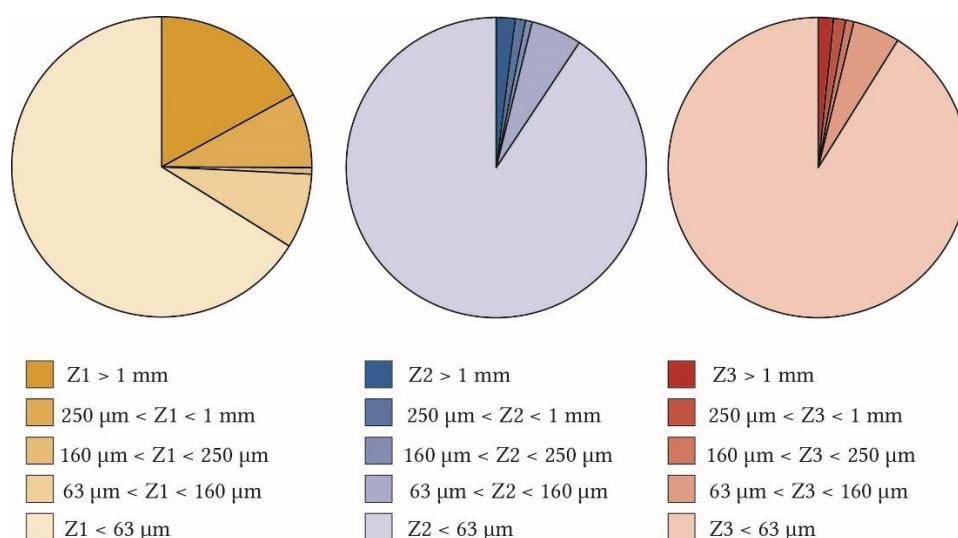


Figure S3. 2: Relative distribution of total organic carbon (mg) in the 5 grain-size fractions of Z1, Z2 and Z3 sediment samples.

Table S3. 2: Pharmaceutical product concentrations measured in dried surface sediments bulk and <63µm grain-size fractions after the wet-sieving procedure using ultra-pure water, and pharmaceutical product concentrations measured in the pond water collected at the water/sediment interface, and in the water collected by centrifugation of the <6 3µm grain-size fraction after the wet-sieving procedure. LOD = limit of detection, LOQ = limit of quantification.

		Tramadol	Paracetamol	Carbamazepine	Oxazepam	Diazepam	Diclofenac
Concentration in the particulate phase (ng/g)							
Bulk sediment	Z1	8	1	85	120	66	<LOD
	Z2	27	1	55	54	43	<LOD
	Z3	32	2	40	45	29	<LOD
<63 µm grain-size fraction	Z1	45	2	31	78	39	<LOD
	Z2	50	1	16	47	28	<LOD
	Z3	27	1	14	22	15	<LOD
LOD (ng/g)		0.2	0.2	0.3	0.4	0.3	0.2
LOQ (ng/g)		0.7	0.6	0.8	1.3	0.8	0.5
Concentration in the dissolved phase (ng/L)							
Pond water	Z1	47	14	886	948	193	14
	Z2	40	15	796	828	141	11
	Z3	39	14	782	854	137	10
Water collected after wet-sieving procedure	Z1	4	2	342	560	149	5
	Z2	6	<LOQ	269	438	154	5
	Z3	7	4	223	323	117	14
LOD (ng/L)		0.7	0.8	0.4	1.3	0.4	0.9
LOQ (ng/L)		2.3	2.3	1.1	3.8	1.1	2.8

The quantification of PPs in the bulk and fine grain-size fractions for Z1, Z2 and Z3 highlighted higher concentrations in CBZ, OXA and DIA in the bulk fraction than in the fine one, suggesting that another grain-size fraction than the fine one might be concentrated in neutral PPs. In the case of TRA, the concentrations were higher in the fine grain-size fraction.

Furthermore, the concentrations in PPs quantified in the water collected at the end of the wet-sieving procedure, by centrifuging the finer grain-size fraction, exhibited concentrations in PPs reaching the same order of magnitude than PPs concentrations in pond water, suggesting that a desorption of PPs occurred during wet-sieving, at least in the case of CBZ, OXA and DIA. The ultra-pure water used for the wet-sieving procedure was evidently free of PPs.

A first hypothesis explaining these relatively high concentrations in PPs in the water collected after the wet-sieving procedure is the desorption of PPs due to the oxidative property of ultra-pure water and the probable weak bonds between surface sediments and PPs. A second hypothesis was the contribution of interstitial water contained in wet-sediment, likely to be also concentrated in PPs, although it doesn't fully explain the mass-balance, suggesting other mechanisms such as desorption from surface sediments during the wet-sieving procedure.

In order to evaluate in general, the role played by organic matter content, composition and reactive character in PPs adsorption or desorption, in the different grain-size fraction of surface sediments, another wet-sieving procedure was employed, using either ultra-pure or pond water. This procedure was performed on delta (=Z1) surface sediments, since the present test allowed to identify a particularly heterogeneous grain-size distribution of TOC in this area, and was presented in Chapter 4.

Supplementary Materials

Pharmaceutical products in pond sediments:
composition, typology and reactivity of
sedimentary organic matter

Number of Tables: 4

Number of Figures: 6

Table S4. 1: Rock-Eval parameters measured after wet-sieving procedure using ultra-pure or pond water. The quantified parameters were the S2 peak (mgHC/g dried sediment), total organic carbon (TOC) content (% and mg), and the hydrogen index (HI, gHC/gTOC). HC = hydrocarbon. R1, R2 and R3 correspond to the replicates.

	Wet-sieving procedure using ultra-pure water					Wet-sieving procedure using pond water				
	Total dry mass (mg)	S2 (mgHC/g dried sediment)	TOC (%)	TOC (mg)	HI (mgHC/gTOC)	Total dry mass (mg)	S2 (mgHC/g dried sediment)	TOC (%)	TOC (mg)	HI (mgHC/gTOC)
Z1 > 1 mm R1	2020	141	24.7	499	570	2470	135	23.2	573	583
Z1 > 1 mm R2		141	23.9	483	588		132	22.1	545	599
Z1 > 1 mm R3		140	24.2	488	578		135	22.6	559	598
250 µm < Z1 < 1 mm	1511	131	22.5	340	580	1121	129	22.8	255	566
160 µm < Z1 < 250 µm	266	127	28.7	76	444	413	115	28.0	115	412
63 µm < Z1 < 160 µm	2968	58	14.1	419	408	3508	59	14.7	515	402
Z1 < 63 µm R1	19,053	50	11.7	2232	429	19,410	50	11.9	2316	420
Z1 < 63 µm R2		50	11.6	2215	427		50	11.9	2312	421
Z1 < 63 µm R3		50	11.9	2274	420		51	11.9	2312	428

Table S4. 2: Gaussian deconvolution parameters, including the baseline y_0 , the height of the curve's peak A , the standard deviation w and the position of the peak's centre x_c , calculated for the four fractions F1 to F4 of the S2 curves with Origin. The relative area of each fraction (%) was also calculated.

		y_0	A	w	x_c	Area %
Z1 > 1 mm	F1	$1,732 \pm 70$	$2,496,631 \pm 26$	68.7 ± 0.6	305.6	13.7
Wet-sieving	F2	$1,732 \pm 70$	$6,067,062 \pm 6$	72.6 ± 0.4	370.2	33.2
Ultra-pure water	F3	$1,732 \pm 70$	$6,886,088 \pm 11$	96.6 ± 1.1	438.4	37.7
	F4	$1,732 \pm 70$	$2,818,396 \pm 70$	89.2 ± 0.8	483.1	15.4
Z1 > 1 mm	F1	$1,454 \pm 64$	$2,425,870 \pm 2,493$	69.2 ± 0.6	305.6	13.7
Wet-sieving	F2	$1,454 \pm 64$	$6,152,160 \pm 559$	74.3 ± 0.4	370.2	34.7
Pond water	F3	$1,454 \pm 64$	$6,391,508 \pm 989$	95.3 ± 1.0	438.4	36.0
	F4	$1,454 \pm 64$	$2,759,939 \pm 604$	88.1 ± 0.7	483.1	15.6
Z1 < 63 μm	F1	814 ± 30	$852,478 \pm 18,770$	69.0 ± 0.8	305.6	12.8
Wet-sieving	F2	814 ± 30	$2,149,990 \pm 36,013$	89.6 ± 1.4	370.2	32.2
Ultra-pure water	F3	814 ± 30	$1,359,051 \pm 32,402$	82.9 ± 1.3	438.4	20.4
	F4	814 ± 30	$2,314,063 \pm 17,208$	81.8 ± 0.4	483.1	34.6
Z1 < 63 μm	F1	694 ± 26	$730,463 \pm 18,237$	70.9 ± 0.8	305.6	12.0
Wet-sieving	F2	694 ± 26	$1,974,520 \pm 35,582$	91.9 ± 1.6	370.2	32.6
Pond water	F3	694 ± 26	$1,189,562 \pm 30,093$	84.1 ± 1.3	438.4	19.6
	F4	694 ± 26	$2,170,461 \pm 15,343$	82.7 ± 0.3	483.1	35.8

Table S4. 3: Concentrations in tramadol (TRA), fluoxetine (FLX), venlafaxine (VFX), carbamazepine (CBZ), oxazepam (OXA) and diazepam (DIA) quantified in bulk sediment (ng/g), in the coarser (i.e. >1 mm) and the finer (i.e. <63 µm) grain-size fractions, in the waters used for the wet-sieving procedure (ng/L) and in the waters collected after the wet-sieving procedure (ng/L). PPs total mass in the waters used for the wet-sieving procedure (ng/L) and in the waters collected after the wet-sieving procedure were also calculated (ng). The mass error was estimated after the error on the water volume used and collected (~5 %). LOD = limit of detection, LOQ = limit of quantification. R1, R2 and R3 correspond to the replicates.

	TRA	FLX	VFX	CBZ	OXA	DIA
PPs concentrations in bulk sediment (ng/g)						
Z1 R1	1.9	8.9	0.6	52.9	222.2	67.8
Z1 R2	2.5	6.7	0.6	49.8	193.3	76.5
Z1 R3	1.0	4.8	<LOQ	47.8	285.7	118.5
Mean value	1.8	6.8	-	50.2	233.7	87.6
Standard deviation	0.8	2.1	-	2.6	47.3	27.1
PPs concentrations in sediment grain size fractions after wet-sieving procedure using pond water (ng/g)						
Z1 < 63µm R1	1.0	2.1	<LOQ	16.9	106.9	28.2
Z1 < 63µm R2	1.0	2.0	<LOQ	18.1	122.9	49.3
Z1 < 63µm R3	1.7	2.7	<LOQ	18.1	142.1	56.6
Mean value	1.2	2.3	-	17.7	124.0	44.7
Standard deviation	0.4	0.4	-	0.7	17.6	14.7
Z1 > 1mm R1	4.3	21.3	5.3	92.9	492.4	185.8
Z1 > 1mm R2	6.4	17.5	8.7	92.8	441.0	172.7
Z1 > 1mm R3	6.0	20.6	7.6	103.8	490.8	179.7
Mean value	5.6	19.8	7.2	96.5	474.7	179.4
Standard deviation	1.1	2.0	1.7	6.3	29.2	6.6
PPs concentrations in sediment grain size fractions after wet-sieving procedure using ultra-pure water (ng/g)						
Z1 < 63µm R1	0.7	1.3	<LOD	11.2	103.7	38.5
Z1 < 63µm R2	0.7	2.3	<LOD	11.4	114.7	45.6
Z1 < 63µm R3	<LOQ	2.2	<LOQ	11.9	126.1	39.6
Mean value	0.7	1.9	-	11.5	114.8	41.2
Standard deviation	0.0	0.6	-	0.3	11.2	3.8
Z1 > 1mm R1	5.9	28.3	6.8	100.6	596.4	227.8
Z1 > 1mm R2	5.8	19.9	5.9	99.9	617.6	266.1
Z1 > 1mm R3	5.7	18.3	5.9	90.1	650.5	257.1

Mean value	5.8	22.2	6.2	96.9	621.5	250.4
Standard deviation	0.1	5.4	0.5	5.9	27.3	20
PPs concentration in water used for the wet-sieving procedure and collected (ng/L)						
Pond water used	37.3	<LOD	56.6	283.7	442.2	72
Water collected after the wet-sieving procedure using pond water	11.4	<LOD	8.8	393.8	641.5	188.5
Water collected after the wet-sieving procedure using ultra-pure water	<LOQ	<LOD	<LOD	191.7	538.9	86
PPs total mass in water before and after the wet-sieving procedure using pond water (ng)						
Pond water used	178.9	<LOD	271.7	1361.9	2122.5	345.4
Error	7.5	-	11.3	56.7	88.4	14.4
Water collected	51.4	<LOD	39.6	1771.9	2886.9	848.5
Error	2.3	-	1.8	78.8	128.3	37.7
PPs total mass difference	-127.5	<LOD	-232.1	410.1	764.3	503.1
Error	7.8	-	11.5	97.1	155.8	40.4
PPs total mass in water before and after the wet-sieving procedure with ultra-pure water (ng)						
Ultra-pure water used	0.0	0.0	0.0	0.0	0.0	0.0
Water collected	<LOQ	<LOD	<LOD	862.8	2425.1	386.9
Error	-	-	-	38.3	114.0	18.2
PPs total mass in sediment (equivalent dry mass = 30.8g) before the wet sieving procedure (ng)						
Z1 R1	57.6	275.4	18.7	1628	6243	2087.7
Z1 R2	78.3	204.9	19.8	1535	5954	2356.8
Z1 R3	30.5	146.7	<LOQ	1471	8800	3650.6
Mean value	55.5	209.0	-	1545	7199	2698.4
Standard deviation	24.0	64.4	-	78.9	1456	835.5

Table S4. 4: Limit of detection (LOD) and of quantification (LOQ) in water and sediment for tramadol (TRA), fluoxetine (FLX), venlafaxine (VFX), carbamazepine (CBZ), oxazepam (OXA) and diazepam (DIA).

		TRA	FLX	VFX	CBZ	OXA	DIA
Water	LOD (ng/L)	0.8	3.5	0.3	0.5	2.0	1.0
	LOQ (ng/L)	2.3	10.4	0.9	1.4	6.1	3.1
Sediment	LOD (ng/g)	0.2	0.2	0.2	0.3	0.4	0.3
	LOQ (ng/g)	0.7	0.6	0.5	0.8	1.3	0.8

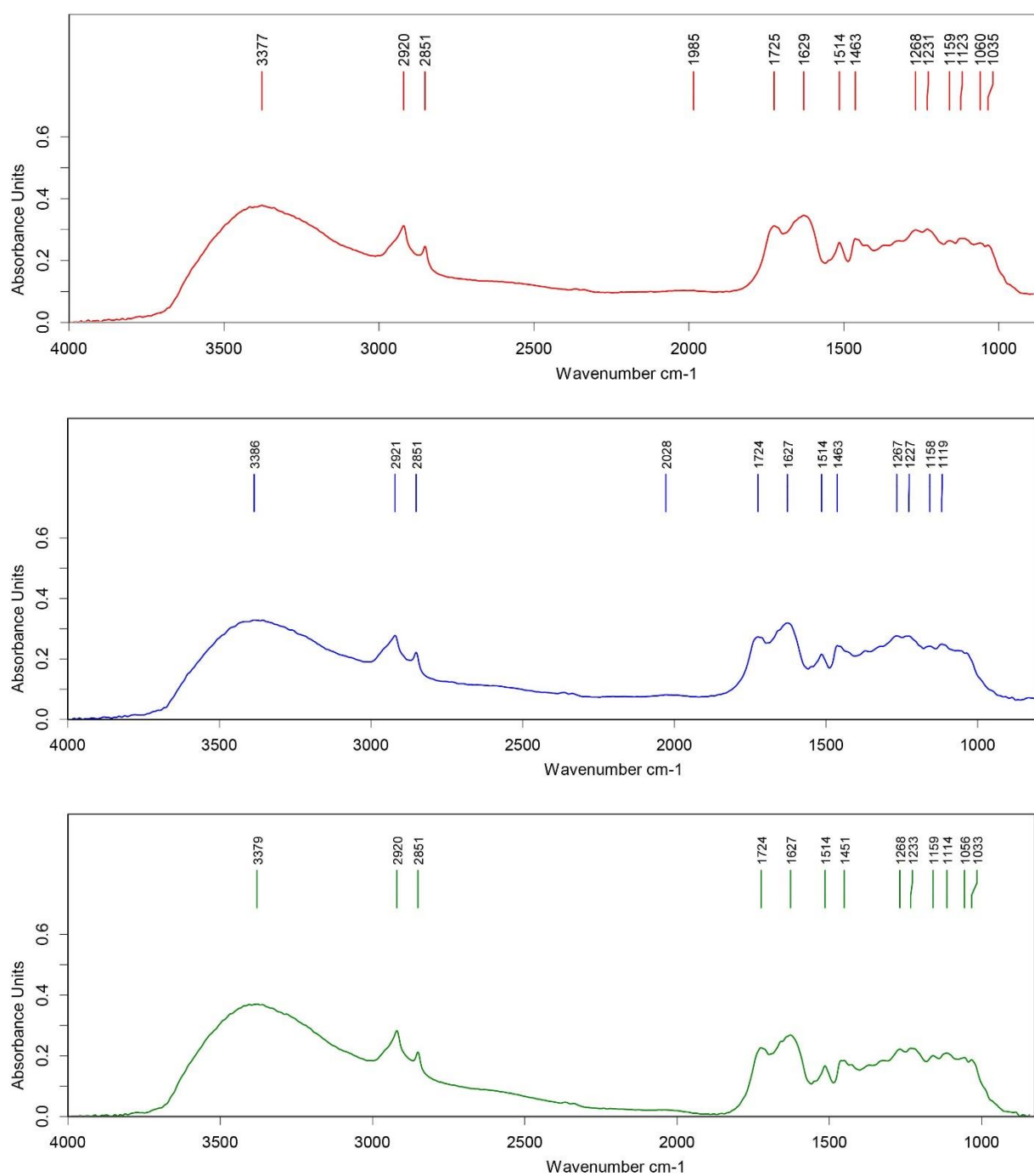


Figure S4. 1: FTIR spectra obtained for the >1 mm grain-size fraction of surface sediments. Spectra were measured in triplicate, by performing the analysis at three different locations on the pellet. The number of scans for each spectrum was 128. Spectra were post-processed using baseline correction on OPUS 7.5 (Bruker).

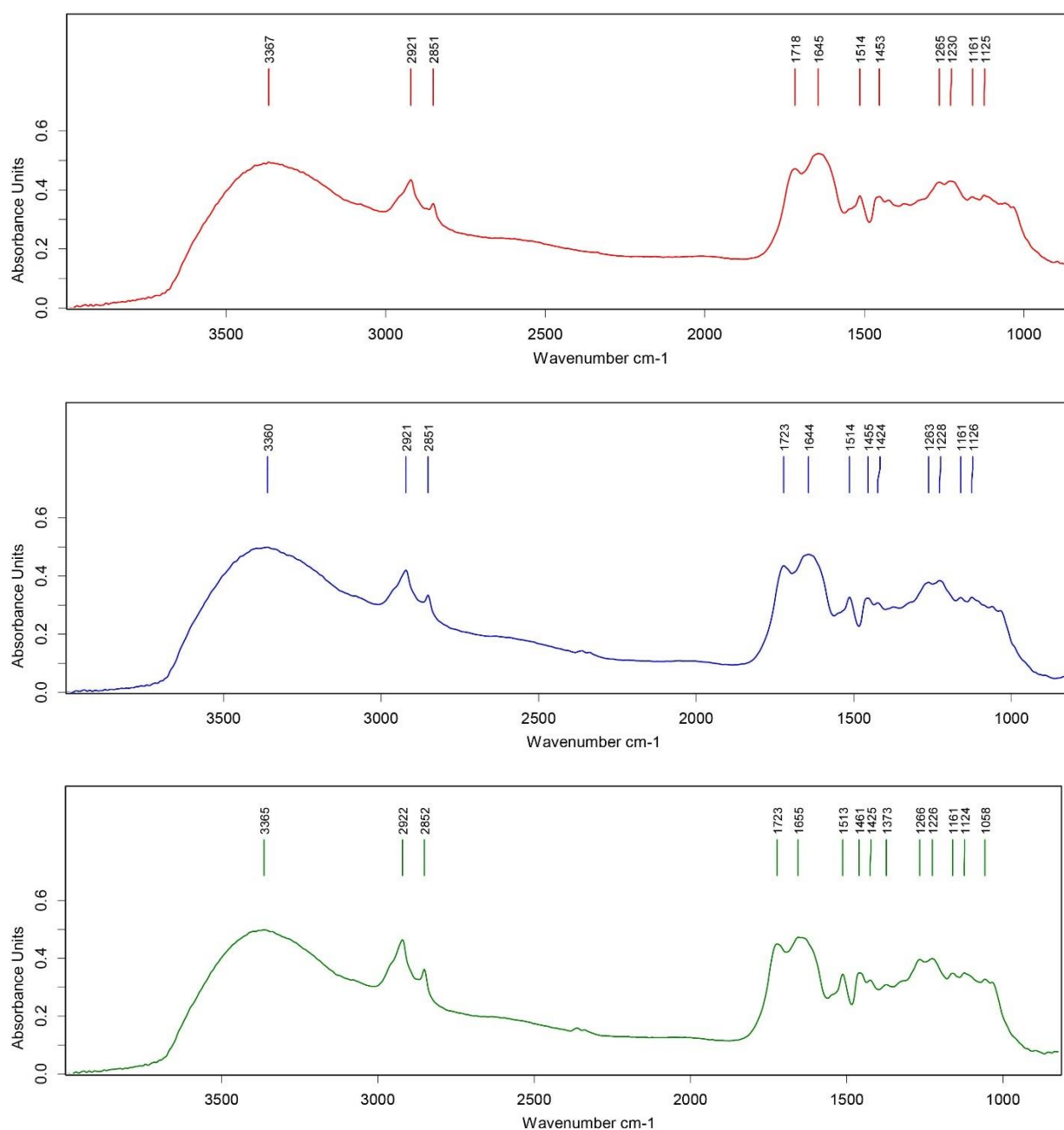


Figure S4. 2: FTIR spectra obtained for the **250 μm -1 mm** grain-size fraction of surface sediments. Spectra were measured in triplicate, by performing the analysis at three different locations on the pellet. The number of scans for each spectrum was 128. Spectra were post-processed using baseline correction on OPUS 7.5 (Bruker).

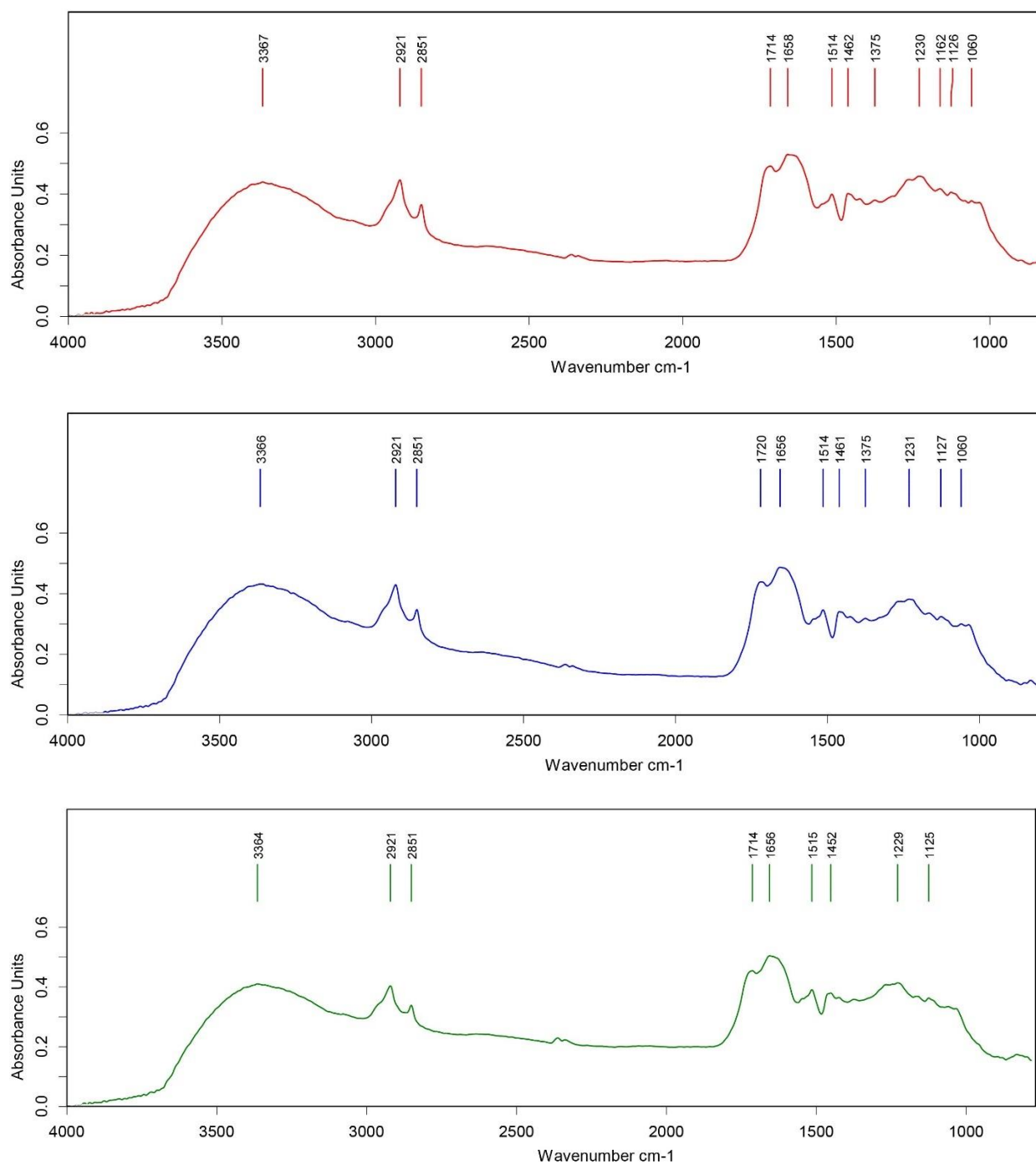


Figure S4. 3: FTIR spectra obtained for the **160 μm -250 μm** grain-size fraction of surface sediments. Spectra were measured in triplicate, by performing the analysis at three different locations on the pellet. The number of scans for each spectrum was 128. Spectra were post-processed using baseline correction on OPUS 7.5 (Bruker).

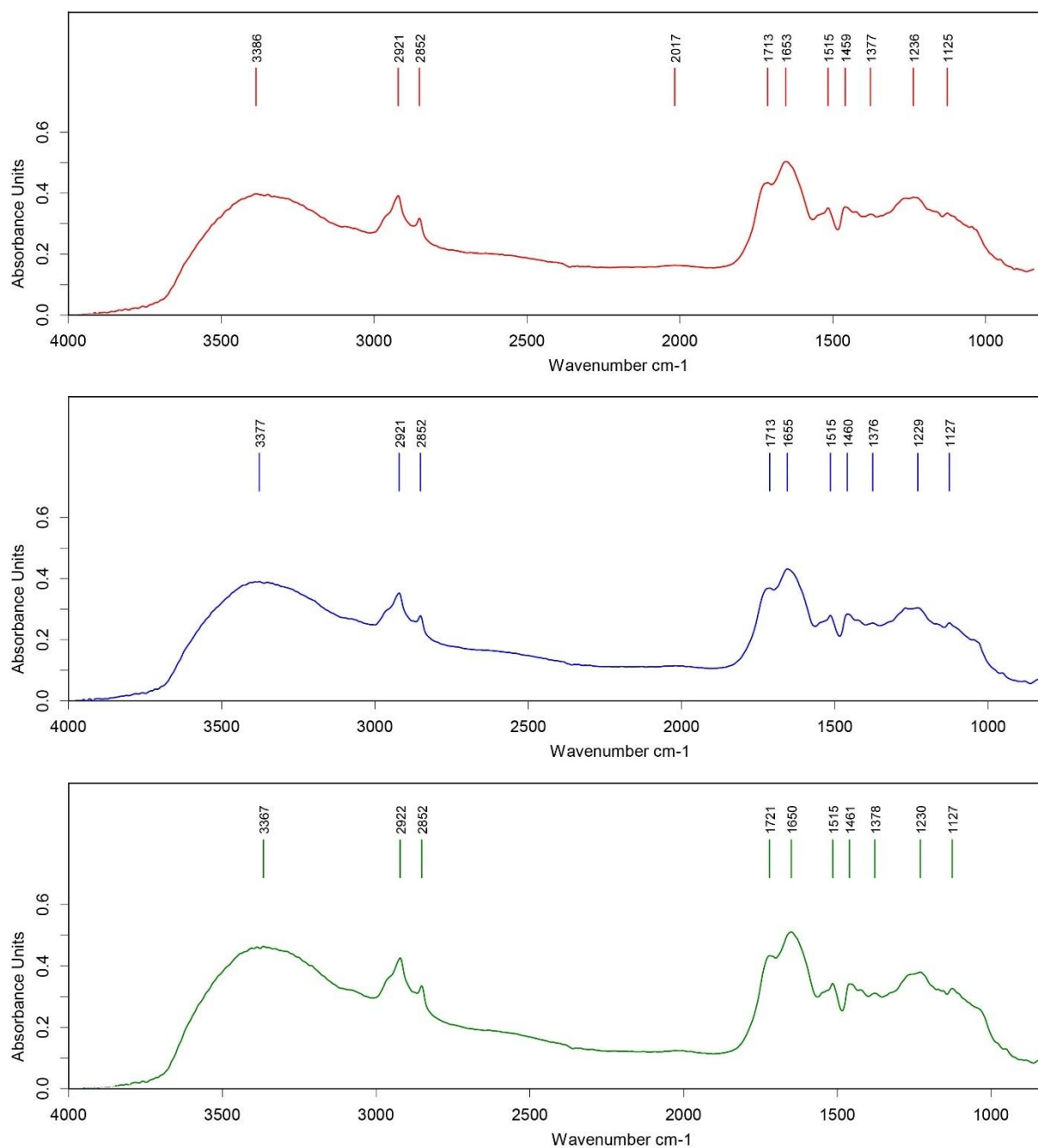


Figure S4. 4: FTIR spectra obtained for the 63 μm -160 μm grain-size fraction of surface sediments. Spectra were measured in triplicate, by performing the analysis at three different locations on the pellet. The number of scans for each spectrum was 128. Spectra were post-processed using baseline correction on OPUS 7.5 (Bruker).

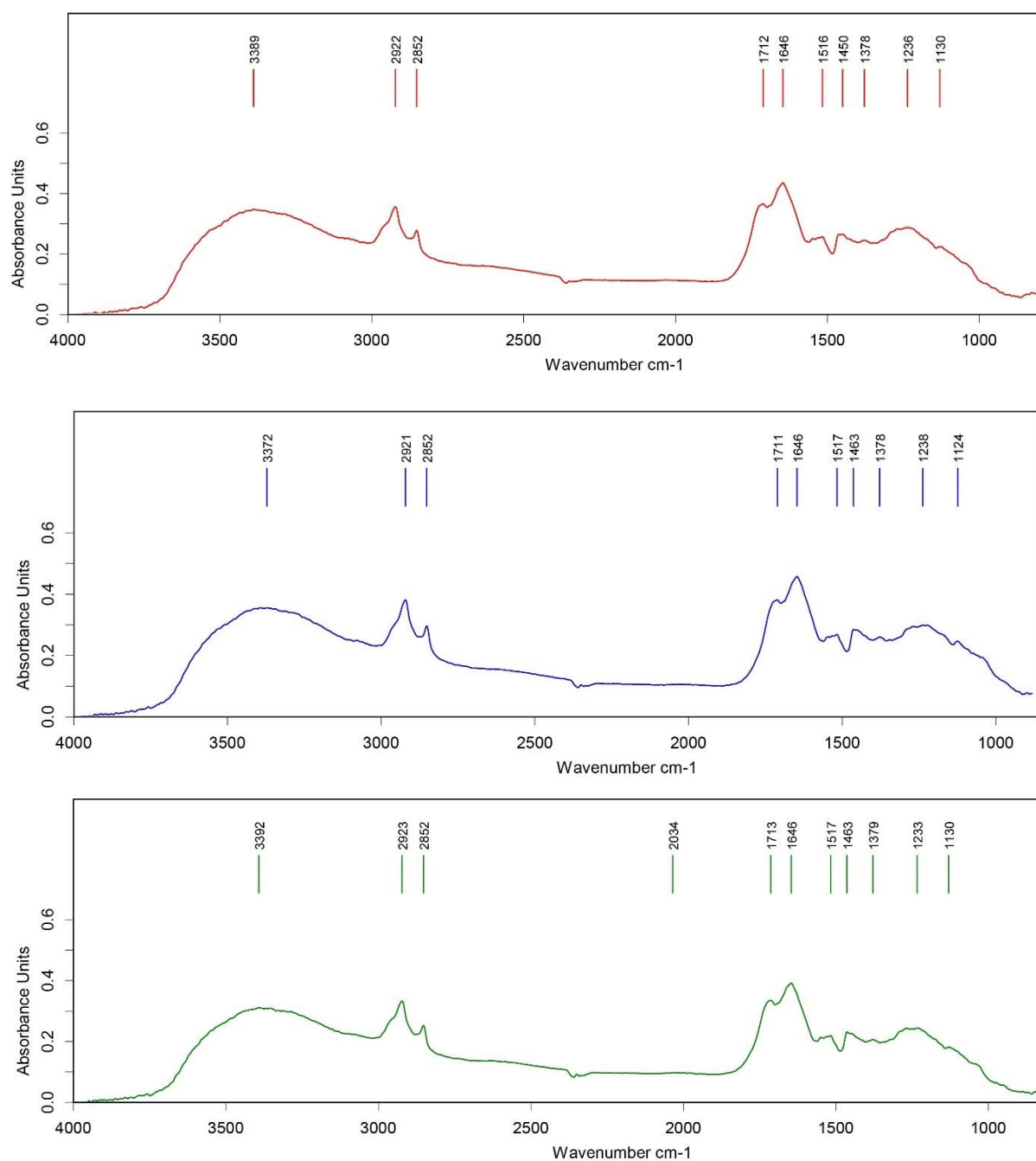


Figure S4. 5: FTIR spectra obtained for the <63 μm grain-size fraction of surface sediments. Spectra were measured in triplicate, by performing the analysis at three different locations on the pellet. The number of scans for each spectrum was 128. Spectra were post-processed using baseline correction on OPUS 7.5 (Bruker).

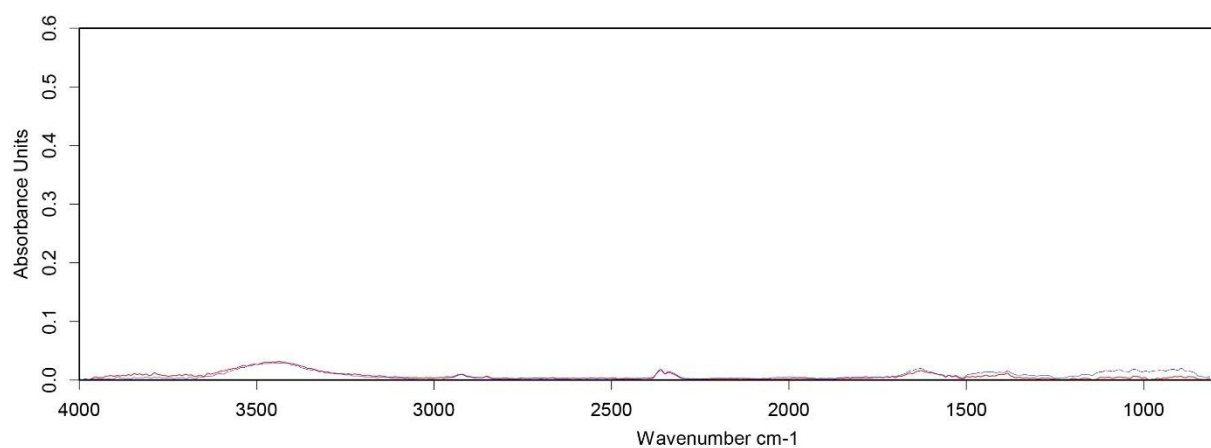


Figure S4. 6: FTIR spectra obtained for the KBr pellets used as background for sample spectra. The number of scans for each spectrum was 128. Spectra were post-processed using baseline correction on OPUS 7.5 (Bruker).

Appendix 5: Composition of the Beulie pond water/sediment interface water in major anions and cations

Methodology: Water-column composition in major anions and cations: ionic chromatography analysis:

Major elements quantification was performed on the water samples collected at the sediment-water interface of the three areas. Samples were previously filtered at 0.45 μm , and samples dedicated to cations analysis were acidified with 1M nitric acid, in order to reach a nitric concentration of 0.01 M. After conditioning, samples were stored at 4 °C until analysis. The day of the analysis, both anions and cations were diluted by a factor 3, using ultra-pure water for anions and a 0.01 M nitric acid solution for cations.

For cations quantification, the machine blank samples were a 0.01 M nitric acid solution, and the field blank samples were ultra-pure water from the field (filtered and unfiltered) and from the ultra-pure water distributor, acidified at 0.01 M nitric acid. The standard used for the calibration was an IC multi-element standard solution (Merck). The standard used as a control point was an inhouse standard. The quantified cations were sodium, ammonium, potassium, magnesium and calcium.

For anions quantification, the machine blank samples were ultra-pure water, and the field blank samples were ultra-pure water from the field (filtered and unfiltered) and from the ultra-pure water distributor. The standard used for the calibration was a multi-element standard solution (Reagecon). The standard used as a control point was an inhouse standard. The quantified anions were fluoride, chloride, nitrite, phosphate and nitrate (Table S5.1).

Table S5. 1: Composition of Beulie pond water in major anions and cations and regression parameters. n.d = not determined; () = out of range or below detection limit; LOD = limit of detection; LOQ = limit of quantification.

	Major anions concentration (mg/L)					Major cations concentration (mg/L)				
	Chlorides	Nitrites	Sulphates	Nitrates	Phosphates	Sodium	Ammonium	Potassium	Magnesium	Calcium
Z1 = delta	17.1	n.d.	11.2	2.3	(3)	16.53	(0.05)	3.34	2.15	31.7
Z2 = upstream area	17.2	n.d.	11.7	2.7	(2.8)	16.65	(0.03)	3.25	2.16	32.1
Z3 = main decantation basin	17.5	n.d.	11.7	2.4	(3)	16.53	(0.04)	3.20	2.15	31.8
Regression parameters										
Calibration range	0.5 – 25 ppm	1.5 – 10 ppm	0.5 – 5 ppm	0.1 – 8 ppm	0.2 – 4 ppm	0.1 – 20 ppm	0.1 – 2 ppm	0.25 – 5 ppm	0.25 – 5 ppm	0.5 – 25 ppm
	Area = 0.173*conc (ppm) - 0.027 R ² = 0.9993	Area = 0.08*conc (ppm) + 0.027 R ² = 0.9995	Area = 0.121*conc (ppm) - 0.02 R ² = 0.9989	Area = 0.142*conc (ppm) - 0.021 R ² = 0.9988	Area = 0.039*conc (ppm) - 0.009 R ² = 0.9962	Area = 0.259*conc (ppm) - 0.016 R ² = 1	Area = 0.248*conc (ppm) + 0.007 R ² = 0.9965	Area = 0.163*conc (ppm) - 0.014 R ² = 1	Area = 0.459*conc (ppm) - 0.093 R ² = 0.9992	Area = 0.3*conc (ppm) - 0.099 R ² = 1
Blank method										
LOD (mg/L)	0.22	n.d.	0.22	0.20	0.28	0.07	n.d.	0.09	0.21	0.34
LOQ (mg/L)	0.33	n.d.	0.27	0.29	0.38	0.07	n.d.	0.09	0.21	0.36
Linearity method										
LOD (mg/L)	0.28	0.17	0.10	0.12	0.16	0.02	0.06	0.01	0.07	0.07
LOQ (mg/L)	0.94	0.57	0.57	0.38	0.54	0.06	0.20	0.05	0.23	0.22

Appendix 6: Supplementary Materials of Chapter 5

Number of Tables: 4

Number of Figures: 2

Table S6. 1: Concentrations in paracetamol (PAR) and diclofenac (DIC) quantified in bulk sediment (ng/g), in the coarser (i.e. >1 mm) and the finer (i.e. <63 µm) grain-size fractions, in the waters used for the wet-sieving procedure (ng/L) and in the waters collected after the wet-sieving procedure (ng/L). PPs total mass in the waters used for the wet-sieving procedure (ng/L) and in the waters collected after the wet-sieving procedure were also calculated (ng). The mass error was estimated after the error on the water volume used and collected (~5%). LOD = limit of detection, LOQ = limit of quantification. R1, R2 and R3 correspond to the replicates.

	PAR	DIC
PPs concentrations in bulk sediment (ng/g)		
Z1 R1	5.1	3.2
Z1 R2	4.2	3.8
Z1 R3	3.9	3.2
Mean value	4.4	3.4
Standard deviation	0.6	0.3
PPs concentrations in sediment grain size fractions after wet-sieving procedure using pond water (ng/g)		
Z1 < 63 µm R1	2.4	12.9
Z1 < 63 µm R2	3.2	4.3
Z1 < 63 µm R3	4.2	1.0
Mean value	3.3	6.1
Standard deviation	0.9	6.1
Z1 > 1 mm R1	6.1	5.7
Z1 > 1 mm R2	3.7	5.7
Z1 > 1 mm R3	3.5	6.6
Mean value	4.4	6.0
Standard deviation	1.5	0.5
PPs concentrations in sediment grain size fractions after wet-sieving procedure using ultra-pure water (ng/g)		
Z1 < 63 µm R1	1.8	<LOD
Z1 < 63 µm R2	1.8	1.5
Z1 < 63 µm R3	3.4	3.5
Mean value	2.3	2.5
Standard deviation	0.9	1.4
Z1 > 1 mm R1	5.8	13.8
Z1 > 1 mm R2	7.4	10.5
Z1 > 1 mm R3	8.8	13.8
Mean value	7.3	12.7
Standard deviation	1.5	1.9

PPs concentration in water used for the wet-sieving procedure and collected (ng/L)		
Pond water used	39.4	28.4
Water collected after the wet-sieving procedure using pond water	46.1	6.8
Water collected after the wet-sieving procedure using ultra-pure water	5.9	22.5
PPs total mass in water before and after the wet-sieving procedure using pond water (ng)		
Pond water used	189.1	136.5
Error	7.9	5.7
Water collected	207.2	30.7
Error	9.2	1.4
PPs total mass difference	18.2	-105.8
Error	12.1	5.9
PPs total mass in water before and after the wet-sieving procedure with ultra-pure water (ng)		
Ultra-pure water used	0.0	0.0
Water collected	26.8	101.2
Error	1.3	4.8
PPs total mass in sediment (equivalent dry mass = 30.8 g) before the wet sieving procedure (ng)		
Z1 R1	156.1	98.3
Z1 R2	129.0	116.0
Z1 R3	120.1	97.4
Mean value	135.1	103.9
Standard deviation	18.8	10.5

Table S6. 2: Evolution of the concentration in carbamazepine (CBZ), oxazepam (OXA), diazepam (DIA), paracetamol (PAR), tramadol (TRA) and diclofenac (DIC) in the dissolved phase during the kinetic experiment.

Step of sampling	Concentration (ng/L)					
	CBZ	OXA	DIA	PAR	TRA	DIC
T0 (= pond water)	271.5	414.6	204.8	134.4	130.6	72.8
T1 = 10 min	341.1	413.4	360.9	41.0	37.1	82.3
After compensation with 0.15 L of initial pond water	338.1	413.5	354.2	45.0	41.1	81.8
T2 = 30 min	335.1	522.2	429.1	40.3	39.9	32.2
After compensation with 0.15 L of initial pond water	332.4	517.6	419.5	44.3	43.8	33.9
T3 = 60 min	339.1	586.6	429.8	24.5	30.8	126.4

Table S6. 3: Limit of detection (LOD) and of quantification (LOQ) in water and sediment for carbamazepine (CBZ), oxazepam (OXA), diazepam (DIA), paracetamol (PAR), tramadol (TRA) and diclofenac (DIC).

		CBZ	OXA	DIA	PAR	TRA	DIC
Water	LOD (ng/L)	0.5	2.0	1.0	0.8	0.8	0.4
	LOQ (ng/L)	1.4	6.1	3.1	2.3	2.3	1.2
Sediment	LOD (ng/g)	0.3	0.4	0.3	0.2	0.2	0.2
	LOQ (ng/g)	0.8	1.3	0.8	0.6	0.7	0.5

Table S6. 4: Raw carbamazepine absorbance data obtained after the analysis of Batch 1 measured addition samples using UV-Visible Spectrophotometry. AD = Addition. UP = ultra-pure.

Sample ID	Time code	Analysis ID	Absorbance at 285±2 nm	Average	±2σ
QH2O	16:38:06	001.QH2O	0.000	0.000	0.001
	16:45:38	009.QH2O	0.000		
	16:52:38	017.QH2O	0.001		
Batch_1	16:38:41	002.Batch_1	0.122	0.123	0.001
	16:46:14	010.Batch_1	0.123		
	16:53:12	018.Batch_1	0.123		
Batch_1_AD0	16:39:15	003.Batch_1_AD0	0.095	0.094	0.001
	16:46:46	011.Batch_1_AD0	0.094		
	16:53:47	019.Batch_1_AD0	0.094		
Batch_1_AD1	16:39:49	004.Batch_1_AD1	0.488	0.488	0.001
	16:47:20	012.Batch_1_AD1	0.488		
	16:54:19	020.Batch_1_AD1	0.488		
Batch_1_AD2	16:40:21	005.Batch_1_AD2	0.867	0.867	0.001
	16:47:54	013.Batch_1_AD2	0.867		
	16:54:53	021.Batch_1_AD2	0.866		
Batch_1_AD3	16:40:55	006.Batch_1_AD3	1.247	1.247	0.001
	16:48:28	014.Batch_1_AD3	1.247		
	16:55:27	022.Batch_1_AD3	1.248		
UP water	16:41:29	007.EAU	-0.001	-0.001	0.001
	16:49:01	015.EAU	-0.001		
	16:56:02	023.EAU	-0.001		

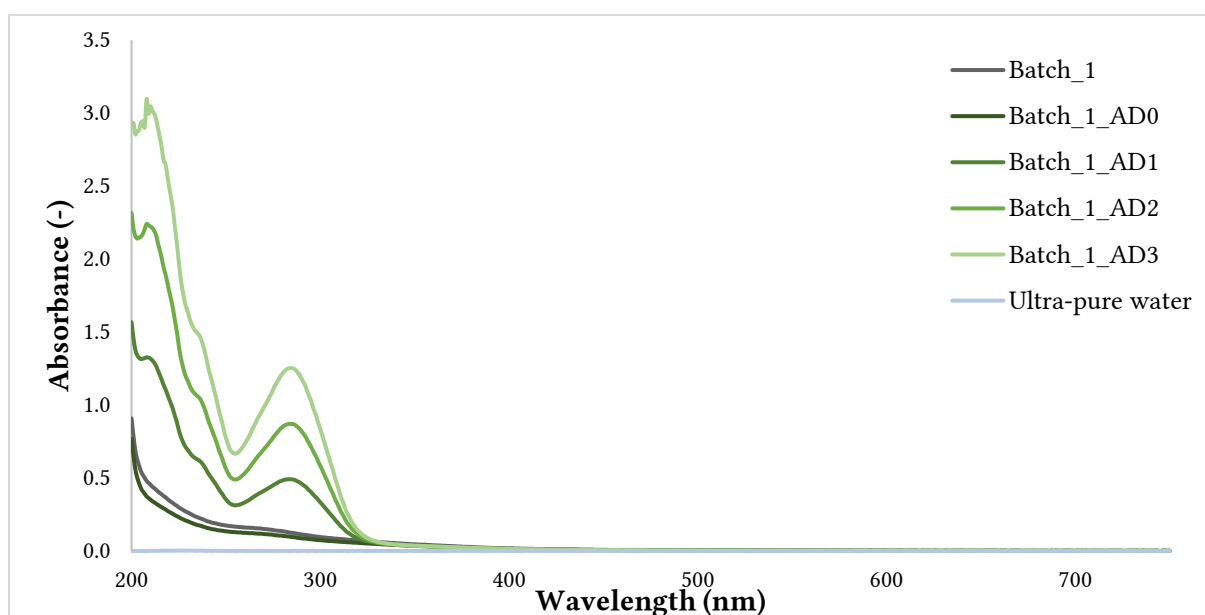


Figure S6. 1: Absorbance spectra of Batch 1 measured addition samples.

Table S6. 5: Calculation of carbamazepine (CBZ) true concentration in Batch 1 using measured addition.

	CBZ added concentration (mg/L)	Absorbance (-)	X residues (%)
AD0	0	0.094	-
AD1	6.67	0.488	-1.49
AD2	13.33	0.867	-0.17
AD3	20	1.247	0.24

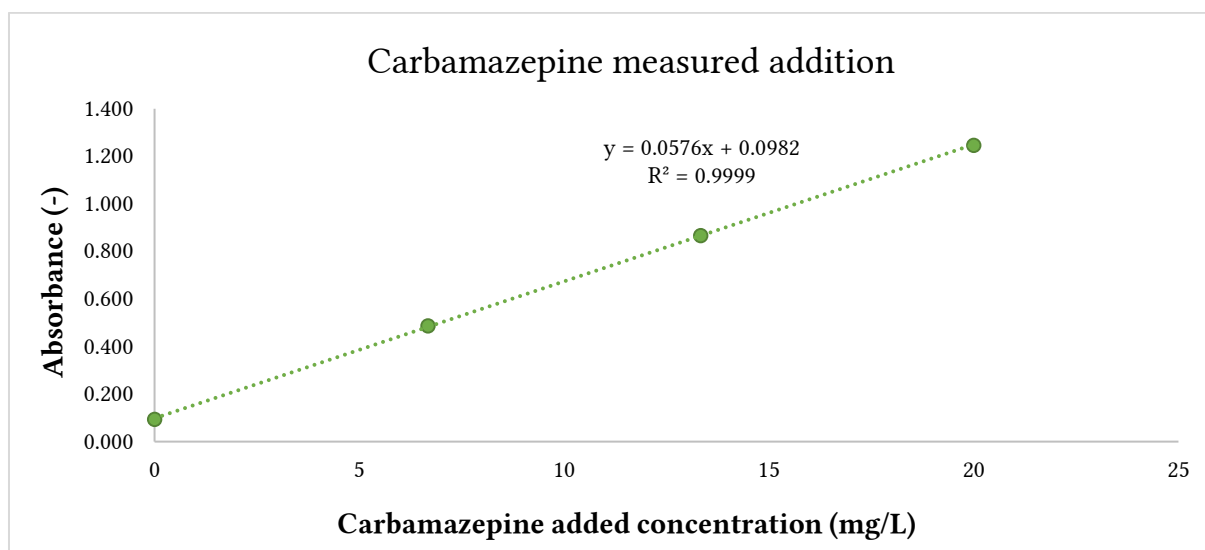


Figure S6. 2: Linear regression of carbamazepine measured addition. Carbamazepine true concentration in Batch 1 is equal to the offset (=slope/intercept), and thus numerically equal to 1.71 mg/L.

This method of measured addition was applied to all blank and batch samples, also in the case of tramadol.

Since Batch 1 corresponds to Beulie surface sediment blank sample, carbamazepine concentration should be close to 0 mg/L (the few ng/g eventually desorbed from surface sediments wouldn't be quantifiable using Spectro UV-Visible Spectrophotometry). The absorbance measured is thus attributable to dissolved phases desorbed from sediment, possibly organic matter fractions.

For this reason, the mean value of the offsets calculated for Blank samples of each categories (sediment, kaolinite, or kaolinite + sediment) were subtracted to the corresponding offsets values calculated for batch samples.

Table S6. 6: Carbamazepine (CBZ) batch samples initial parameters and adsorbed concentrations.

Samples	Sample IDs	Sediment mass (mg)	Kaolinite mass (mg)	Initial CBZ concentration (mg/L)	Offset (mg/L)	Equilibrium CBZ concentration (mg/L)	Adsorbed CBZ concentration (mg/L)	Adsorbed CBZ concentration (%)	Adsorbed CBZ concentration (mg CBZ/g dry solid phase)
BLK_Beulie_R1	Batch_1	200.5	x	0	1.71				
BLK_Beulie_R2	Batch_2	200.2	x	0	1.68				
BLK_Beulie_R3	Batch_3	200.1	x	0	1.63				
BLK_Kaol_R1	Batch_22	x	200.8	0	0.08				
BLK_Kaol_R2	Batch_23	x	199.9	0	0.03				
BLK_Kaol_R3	Batch_24	x	199.3	0	0.04				
BLK_Beulie_Kaol_R1	Batch_4	151	50.8	0	1.2				
BLK_Beulie_Kaol_R2	Batch_5	150.1	50.5	0	1.19				
BLK_Beulie_Kaol_R3	Batch_6	151	50.6	0	1.28				
Batch_Beulie_CBZ_R1	Batch_7	200.8	x	9.96	7.54	5.87	4.09	41.1	0.815
Batch_Beulie_CBZ_R2	Batch_8	200.7	x	9.96	7.68	6.01	3.95	39.7	0.788
Batch_Beulie_CBZ_R3	Batch_9	200.4	x	9.96	8.01	6.34	3.62	36.4	0.723
Batch_Kaol_CBZ_R1	Batch_16	x	200.9	9.96	6.78	6.73	3.23	32.4	0.643
Batch_Kaol_CBZ_R2	Batch_17	x	200.1	9.96	6.73	6.68	3.28	32.9	0.656
Batch_Kaol_CBZ_R3	Batch_18	x	200.6	9.96	6.76	6.71	3.25	32.6	0.648
Batch_Beulie_Kaol_CBZ_R1	Batch_10	150.5	49.7	9.96	7.08	5.86	4.10	41.2	0.820
Batch_Beulie_Kaol_CBZ_R2	Batch_11	150.5	50.4	9.96	7.24	6.02	3.94	39.6	0.785
Batch_Beulie_Kaol_CBZ_R3	Batch_12	149.5	49.6	9.96	7.33	6.11	3.85	38.7	0.774

Table S6. 7: Tramadol (TRA) batch samples initial parameters and adsorbed concentrations.

Samples	Sample IDs	Sediment mass (mg)	Kaolinite mass (mg)	Initial TRA concentration (mg/L)	Offset (mg/L)	Equilibrium TRA concentration (mg/L)	Adsorbed TRA concentration (mg/L)	Adsorbed TRA concentration (%)	Adsorbed TRA concentration (mg TRA/g dry solid phase)
BLK_Beulie_R1	Batch_1	200.6	x	0	18.02				
BLK_Beulie_R2	Batch_2	200.2	x	0	19.08				
BLK_Beulie_R3	Batch_3	200.1	x	0	18.55				
BLK_Kaol_R1	Batch_13	x	200.8	0	0.67				
BLK_Kaol_R2	Batch_14	x	199.9	0	0.9				
BLK_Kaol_R3	Batch_15	x	199.3	0	0.86				
BLK_Beulie_Kaol_R1	Batch_4	150.1	50.5	0	14.47				
BLK_Beulie_Kaol_R2	Batch_5	150.1	49.2	0	13.67				
BLK_Beulie_Kaol_R3	Batch_6	149.6	49.5	0	13.56				
Batch_Beulie_TRA_R1	Batch_7	199.4	x	20.11	27.41	8.86	11.25	55.9	2.257
Batch_Beulie_TRA_R2	Batch_8	201.5	x	20.11	27.85	9.3	10.81	53.8	2.146
Batch_Beulie_TRA_R3	Batch_9	201.3	x	20.11	27.88	9.33	10.78	53.6	2.142
Batch_Kaol_TRA_R1	Batch_19	x	201.1	20.11	14.16	13.35	6.76	33.6	1.345
Batch_Kaol_TRA_R2	Batch_20	x	200.4	20.11	13.68	12.87	7.24	36.0	1.445
Batch_Kaol_TRA_R3	Batch_21	x	200.8	20.11	13.47	12.66	7.45	37.0	1.484
Batch_Beulie_Kaol_TRA_R1	Batch_10	151.2	49.8	20.11	23.98	10.08	10.03	49.9	1.996
Batch_Beulie_Kaol_TRA_R2	Batch_11	150.4	49.8	20.11	23.41	9.51	10.60	52.7	2.118
Batch_Beulie_Kaol_TRA_R3	Batch_12	149.5	50.7	20.11	23.79	9.89	10.22	50.8	2.042

Appendix 7: Adsorption experiment using a reference humic acid and kaolinite

Leonardite humic acid alone:

In order to evaluate the sorption (or complexing) capacity of humic acids, which are largely part of the composition of organic matter (OM), batch experiments were performed with on the one hand a leonardite humic acid solution (1S104H, IHSS, 50 mg/L dissolved organic carbon) in a dialysis bag (Spectrapor VWR, 3.5 kDa) and on the other hand a solution of either carbamazepine (CBZ) or tramadol (TRA). The leonardite solution was prepared by dissolving 78.5 mg of leonardite standard in 1L of a 7.10^{-5} M NaOH solution, since leonardite dissolves under basic conditions. The dialysis bags were firstly carefully rinsed several times using ultra-pure water under a hood, since they are conditioned in sodium azide (NaN_3). Then, 10 mL of the leonardite solution were introduced in the dialysis bag, the latter being finally closed using plastic clamps. Then, dialysis bags were introduced in 250 mL HDPE bottles, filled with 250 mL of either CBZ or TRA 100 $\mu\text{g/L}$ solution. Bottles were collected regularly until 24 h of stirring. 20 mL of the bottle solution was dedicated to pH measurement, 50 mL to DOC analysis and 180mL to PPs quantification using GC-MS analysis (Figure S6.1). The DOC was quantified using TOC-L analyser (Shimadzu) with a high sensitivity method. The pH and the DOC remained constant during the kinetic experiment, ensuring that no leonardite crossed the dialysis bag (Table S7.1).

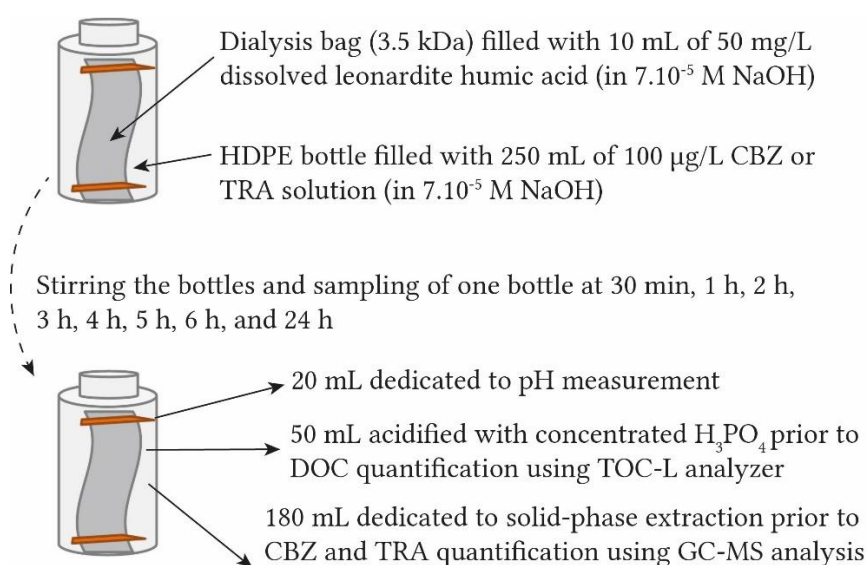


Figure S7. 1: Batch sample preparation including a 3.5 kDa dialysis bag filled with leonardite humic acid solution and a 250 mL HDPE bottle filled with a 100 $\mu\text{g/L}$ solution of either carbamazepine (CBZ) or tramadol (TRA).

Table S7. 1: pH and dissolved organic carbon concentration measured in the aqueous phase of batch samples at each sampling step.

Batch sample (time of sampling)	pH	Dissolved organic carbon concentration (mg/L)
T = 0 min	9.8	0.61±0.15
T = 30 min	9.7	0.65±0.07
T = 1h	9.7	0.65±0.03
T = 2h	9.8	0.60±0.01
T = 3h	9.8	0.63±0.05
T = 4h	9.8	0.81±0.06
T = 5h	9.8	0.67±0.13
T = 6h	9.8	0.59±0.03

Prior to GC-MS quantification, a matrix change was operated with solid-phase extraction (SPE). The procedure is the same than the one used prior the LC-MS/MS analysis (Chapter 2). Water samples are transferred into SPE columns, whom solid phase retains PPs, and PPs are recovered in 10 mL methanol. Then, 50 µL of 5α-cholestane, an internal standard, are added, and methanol is evaporated under nitrogen flux. In order to improve the chromatographic behaviour of molecules, a silylation, which is a derivatization method using MTBSTFA in our case, was employed. Molecules were recovered from glass vials edges after the evaporation of methanol using 60 µL of pyridine. Then, the 60 µL of pyridine were mixed with 40 µL of MTBSTFA in GC-MS glass vials before being heated at 70 °C during 1 h.

The quantification of CBZ and TRA was proceeded by integrating their respective peaks on the total ionic chromatogram (TIC). The corresponding area was divided by the one of the internal standard. Calibration solution of both CBZ and TRA were analysed at the same time than samples. Unfortunately, TRA couldn't be quantified since its characteristic peaks didn't appear on the TIC, due to either extraction or derivatization issues. Regarding the GC-MS response against concentrations of the calibration solutions, a high-range (Figure S7.2, in blue) and a low-range (Figure S7.2, in orange) calibrations were used. According to the CBZ concentration residues calculated after the linear regression, the quantification of CBZ is only available in the 7.5-100 µg/L range, with an accuracy of 9.12 % (Table S7.2).

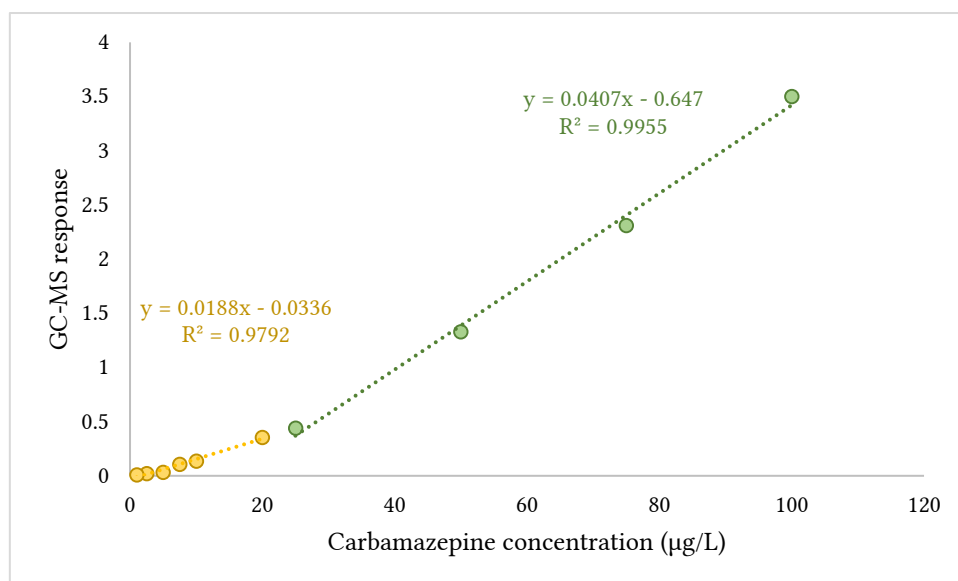


Figure S7. 2: Calibration of carbamazepine (CBZ) with the GC-MS response as a function of the concentration. A low-range (yellow) and a high-range (green) linear regressions were calculated.

Table S7. 2: Carbamazepine concentration residues calculated after low-range and high-range linear regressions.

Low-range calibration		
Concentration (µg/L)	GC-MS response	X residues (%)
1	0.009	-126.8
2.5	0.02	-14.1
5	0.034	-28.0
7.5	0.107	0.15
10	0.137	9.12
20	0.355	-3.5
High-range calibration		
Concentration (µg/L)	GC-MS response	X residues (%)
25	0.439	-6.8
50	1.329	2.8
75	2.311	3.03
100	3.501	-2.0

The evolution of the concentration in CBZ in the bottle fluctuated within the 6 hours of the kinetic experiment, preventing from estimating if a complexation with leonardite humic acid occurs or not (Figure S7.3). Theoretically, the molecular weight of CBZ is far below the cutting size of dialysis bag, which shouldn't prevent CBZ from diffusing inside the dialysis bag.

Another hypothesis is that complexation occurs, although the bonds formed between leonardite humic acid functional group and CBZ are too weak to handle the stirring.

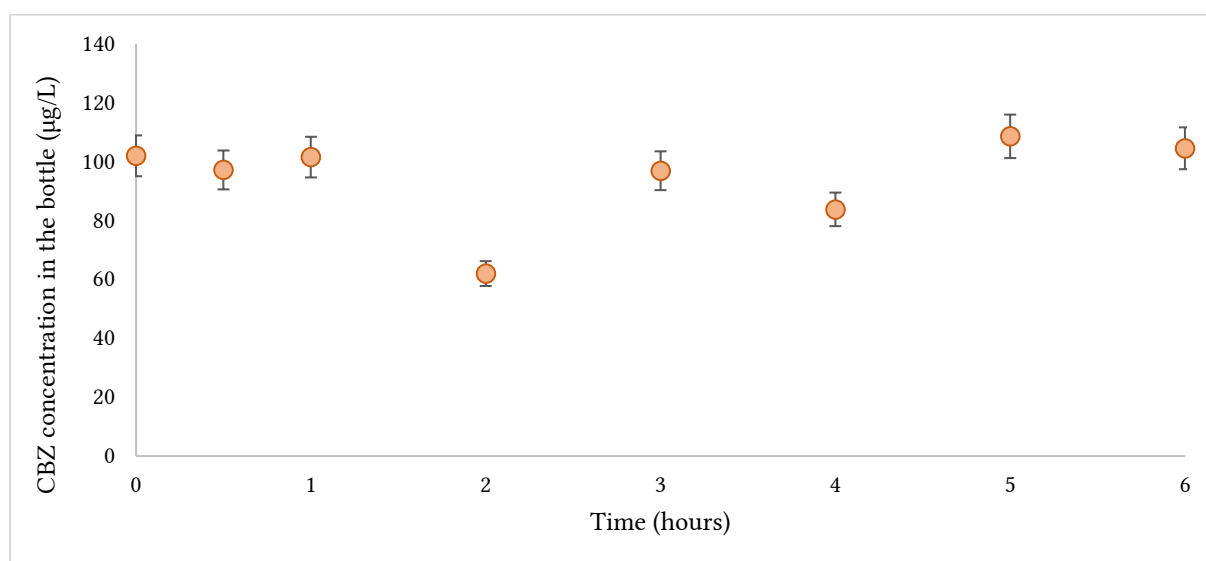


Figure S7. 3: Concentration in carbamazepine (CBZ) in the bottle solution as a function of time. An error of accuracy of 6.8 % was applied to all values, which corresponds to the maximal residues in concentration calculated for the high-range calibration (Table 1).

Leonardite humic acid and kaolinite:

A sorption batch experiment was also performed with kaolinite as the solid phase and with a solution of leonardite humic acid and TRA at different concentrations. The leonardite humic acid was dissolved in an 7.10^{-5} M NaOH solution. The pH of the solution was 8.8. The batches were performed in 15mL plastic tubes, with about 100mg of kaolinite and 10 mL of a leonardite solution (dissolved organic carbon equivalent concentration = 25 mg/L) with increasing TRA concentrations (0-20 mg/L). TRA concentration quantification in batches was proceeded using UV-Visible Spectrophotometry (UVVS). TRA calibration solutions were also prepared in leonardite solution. Preliminary to quantification, leonardite solution was also calibrated using UVVS, in order to determine if its absorbance was evolving linearly with its concentration.

The results of the calibration of DOC concentration in leonardite humic acid confirmed a linear evolution of the absorbance with leonardite humic acid dissolved organic carbon (DOC) concentration (Figure S7.3 and S7.4), and allow the quantification in the range of 5-25 mg/L in DOC with an accuracy of 8.3%, since the concentration residues below 5 mg/L are too high to guarantee a good accuracy (Table S7.3).

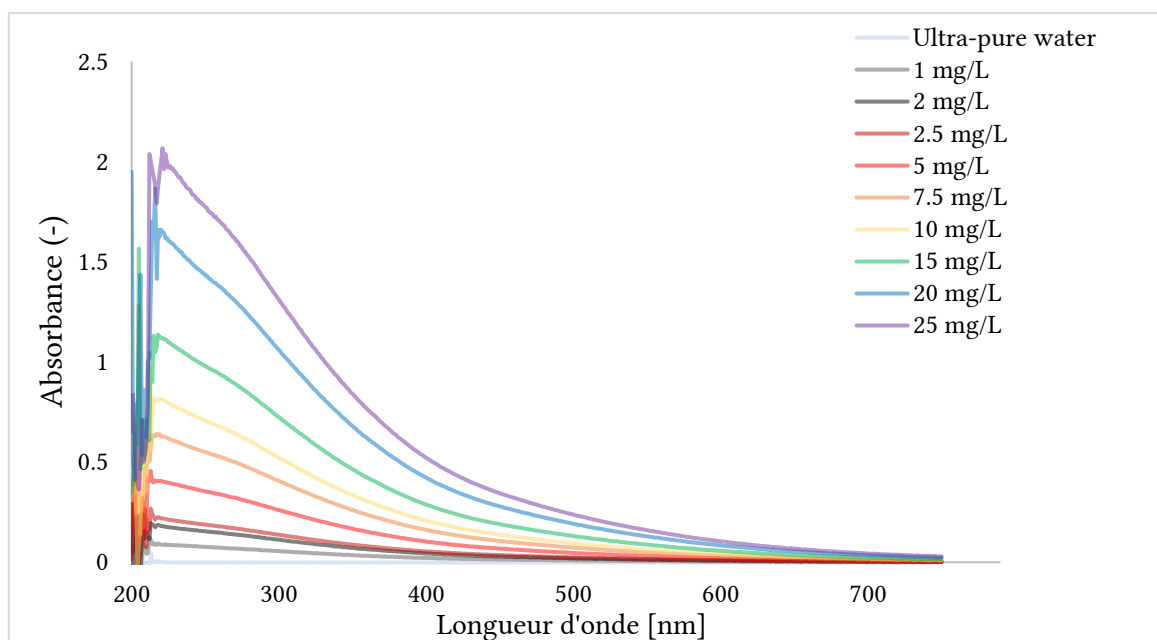


Figure S7. 4: Absorbance spectra of leonardite humic acid measured with UV-Visible Spectrophotometry in the 200-750 nm wavelength range.

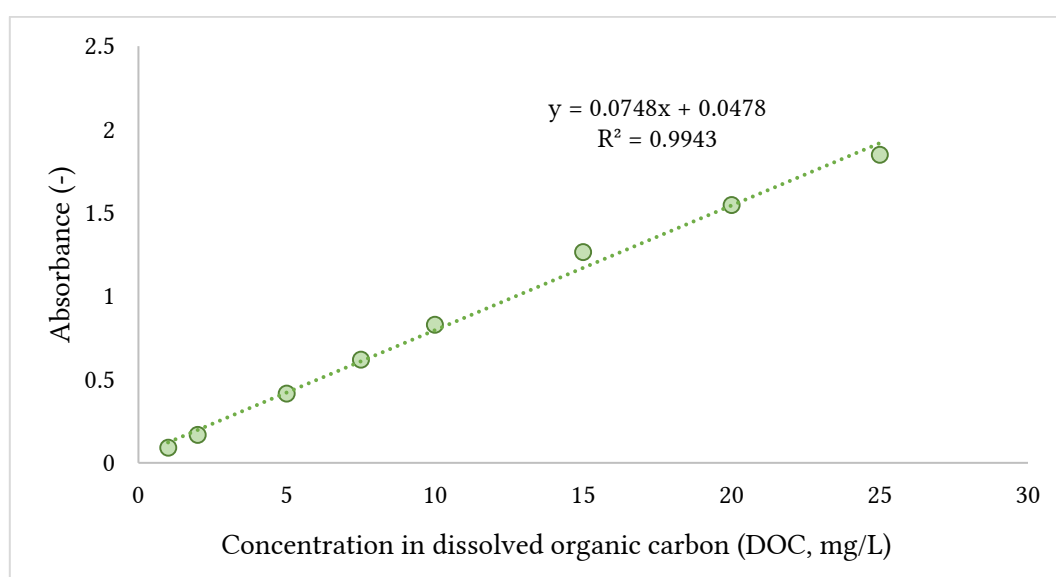


Figure S7. 5: Calibration leonardite humic acid using the absorbance as a function of the DOC concentration. A linear regression was calculated (green line).

Table S7. 3: DOC concentration residues calculated after the linear regression.

Concentration in DOC (mg/L)	Absorbance (chromophore at 218 nm)	Concentration residues (%)
1	0.090	43.5
2	0.167	20.2
5	0.416	1.6
7.5	0.618	-1.7
10	0.828	-4.3
15	1.263	-8.3
20	1.547	-0.2
25	1.849	3.7

The results of the calibration of TRA concentration in leonardite humic acid solution confirmed a linear evolution of the absorbance with TRA concentration (Figure S7.5 and S7.6), and allow the quantification in the range of 2.5-20 mg/L in TRA (Table S7.4), with an accuracy of 10.7%.

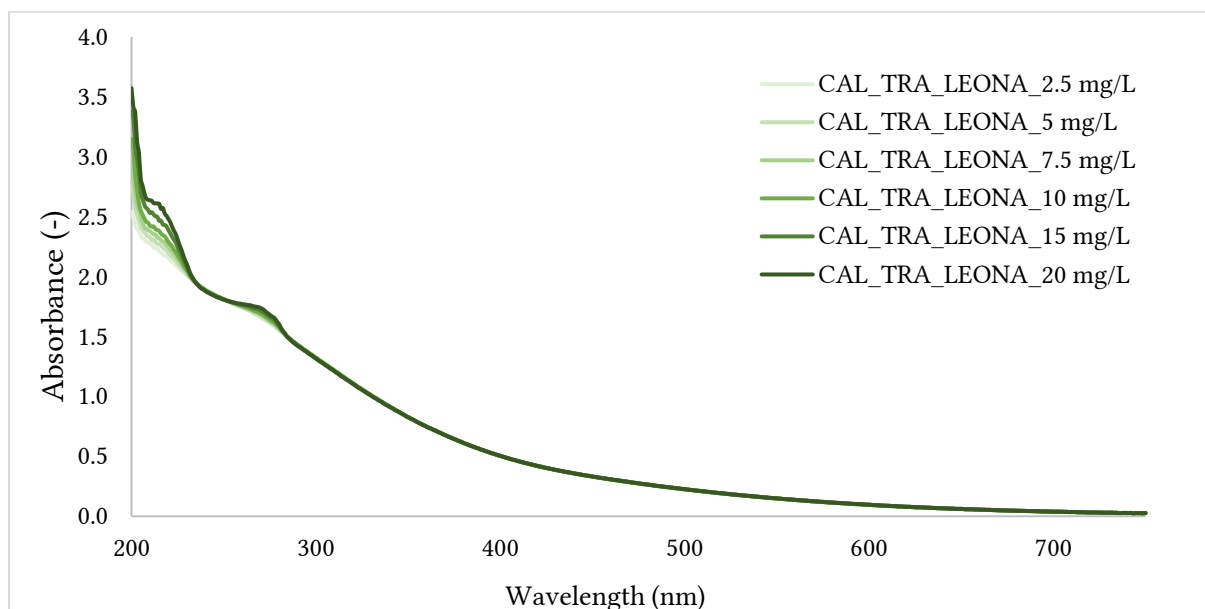


Figure S7. 6: Absorbance spectra of tramadol (TRA) in a leonardite humic acid solution measured with UV-Visible Spectrophotometry in the 200-750 nm wavelength range.

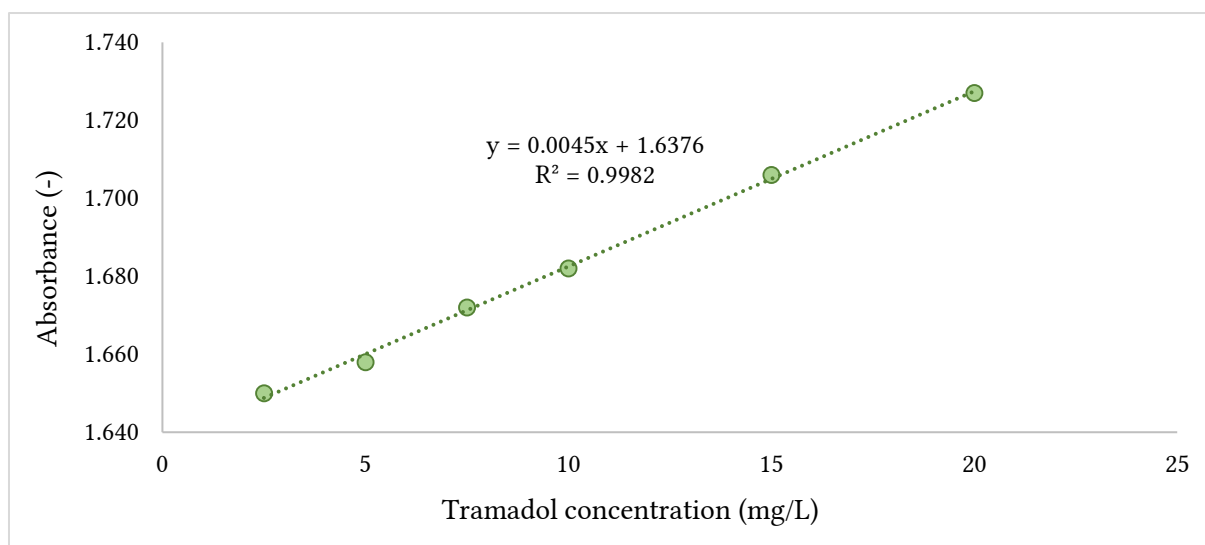


Figure S7. 7: Calibration of tramadol (TRA) using the absorbance as a function of TRA concentration. A linear regression was calculated (green line).

Table S7. 4: Tramadol (TRA) concentration residues calculated after the linear regression.

Concentration in TRA (mg/L)	Absorbance (chromophore at 271 nm)	Concentration residues (%)
2.5	1.650	-10.7
5	1.658	9.0
7.5	1.672	-2.2
10	1.682	1.1
15	1.706	-1.5
20	1.727	0.5

Batch experiment were performed in triplicate, and the pH was measured at equilibrium (Table S6.3). Unfortunately, the quantification of TRA concentration in the solution at equilibrium was compromise by the decrease in pH that caused the partial precipitation of leonardite humic acid. In opposition with the case in which leonardite was the only phase, whitth constant pH (Table S7.1), here kaolinite may have acted as a buffer, inducing a pH decrease (Table S7.5). Thus, the DOC concentration in the solution was not stable during the experiment, which prevented from quantifying TRA in the dissolved phase using the measured absorbance and the calibration.

Table S7. 5: pH measured in the aqueous phase of batch samples at equilibrium.

Batch sample (TRA initial concentration in mg/L)	pH
Batch TRA 2.5 mg/L	6.8
Batch TRA 5 mg/L	6.7
Batch TRA 7.5 mg/L	6.9
Batch TRA 10 mg/L	6.8
Batch TRA 15 mg/L	6.7
Batch TRA 20 mg/L	6.7

This issue might be avoided with the use of a basic buffer in order to keep the pH constant, such as sodium carbonate/bicarbonate ($\text{Na}_2\text{CO}_3/\text{NaHCO}_3$). Furthermore, in complex matrices such as kaolinite + leonardite, the quantification using the measured addition method (cf Chapter 2, Section 8.2) is more accurate, and was therefore used for the other batch experiments (cf Chapter 5).

Amélie HUMBRECHT

Comportement des produits pharmaceutiques dans le continuum eau-sédiments : une approche couplée terrain-laboratoire en contexte périurbain

Le devenir des contaminants émergents constitue aujourd'hui une question majeure dès lors qu'il s'agit de caractériser l'état et les dynamiques des écosystèmes de surface. D'après la bibliographie récente, les écosystèmes les plus sensibles aux nouveaux Polluants Organiques Persistants (POPs), tels que les produits pharmaceutiques (PPs), sont les systèmes hydrologiques de petites tailles, soumis à des rejets d'origine anthropique. Le comportement des PPs, au sein de la matrice particulaire en transit dans ces écosystèmes, et leur devenir dans le continuum eau-sédiments restent un verrou majeur pour établir des bilans de masse précis, ainsi que pour identifier et quantifier leurs niveaux de contamination dans les écosystèmes terrestres et aquatiques. Comprendre le comportement des PPs dans le continuum eau-sédiments s'avère être un enjeu pour 1) déterminer la nature des matrices réactives pour l'adsorption des PPs, 2) comprendre le rôle joué par les facteurs environnementaux, à l'instar des conditions physico-chimiques, dans la diagenèse de la matière organique sédimentaire, matrice ayant une affinité connue pour les PPs et 3) évaluer la stabilité ou la potentielle réversibilité du piégeage des PPs sur la phase particulaire. Dans ce cadre, et basé sur les résultats acquis depuis 2017 sur les matrices eau et sédiment en transit dans le bassin versant de l'Egoutier (Semoy, Loiret, France), ce travail de thèse a pour ambition de suivre le comportement des PPs dans le continuum eau-sédiment de l'étang de la Beulie, afin d'étudier les paramètres et les mécanismes qui régissent leur devenir dans les environnements de surface. Ceci sera rendu possible par un couplage terrain/expérimental et l'analyse de PPs cibles selon les phases porteuses en transfert dans l'hydrosystème Egoutier, avec un intérêt particulier porté sur la matière organique. Les enjeux seront notamment de déterminer la réponse spatiale des PPs à l'échelle de l'étang de la Beulie, de comprendre le comportement des PPs au sein de la matrice sédimentaire en lien avec la composition, la typologie et la réactivité de la matière organique, et d'identifier les mécanismes et les cinétiques d'adsorption des PPs sur la phase particulaire au travers d'expériences en batchs, avec une évaluation de la potentielle réversibilité du piégeage.

Mots clés : produits pharmaceutiques, matière organique, terrain et expériences en laboratoire, étang, interface eau/sédiments, phases porteuses

The behaviour of pharmaceutical products in the water-sediment continuum: a combined field and laboratory approach in a suburban context

The fate of contaminants of emerging concern is one of the major scientific issues related to the characterisation of surface ecosystem quality and dynamics. According to recent literature, small-scale hydrosystems have been found to be particularly sensitive to new persistent organic pollutants (POPs), such as pharmaceutical products (PPs). The behaviour of PPs within the particulate matrix as it is transferred through hydrosystems, and their fate in the water-sediment continuum, are still poorly understood. However, this knowledge is necessary in order to accurately quantify mass balances and identify and quantify rates of PPs contamination in terrestrial and aquatic ecosystems. Understanding the behaviour of PPs in the water-sediment continuum is important for 1/ determining the nature of the reactive matrices likely to carry PPs 2/ understanding the role played by environmental factors, such as physico-chemical conditions, in the diagenesis of sedimentary organic matter (a matrix with a known affinity for PPs) and 3/ evaluating the stability or potential reversibility of PPs being trapped in the particulate phase. In this context, building on results collected since 2017 about the transfer of particulate and aqueous phases through the Egoutier catchment (Semoy, Loiret, France), this PhD work aims to determine the behaviour of PPs in the water-sediment continuum of the Beulie pond, and more particularly to characterise the parameters and mechanisms that influence the fate of PPs in surface environments. This will be achieved through a combined field and laboratory approach, analysing targeted PPs in particulate and aqueous phases. The role of organic matter will be given particular consideration. The study aims to determine the spatial response of PPs at the scale of the Beulie pond, understand the behaviour of PPs within surface sediments collected at the pond's water/sediment interface with regard to the composition, typology, and reactivity of sedimentary organic matter, and identify the mechanisms and kinetics of PPs' sorption to the particulate phase through batch experiments with an evaluation of the potential reversibility of trapping.

Keywords: pharmaceutical products, organic matter, field and laboratory experiments, pond, water/sediment interface, carrier phases

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