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Tom Ducrocq, Sylvain Merel, Cécile Miège. Review on analytical methods and occurrence of organic contaminants in continental water sediments. *Chemosphere*, 2024, 365, pp.143275. 10.1016/j.chemosphere.2024.143275 . hal-04723037

HAL Id: hal-04723037

<https://hal.science/hal-04723037v1>

Submitted on 6 Oct 2024

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Review on analytical methods and occurrence of organic contaminants in continental water sediments

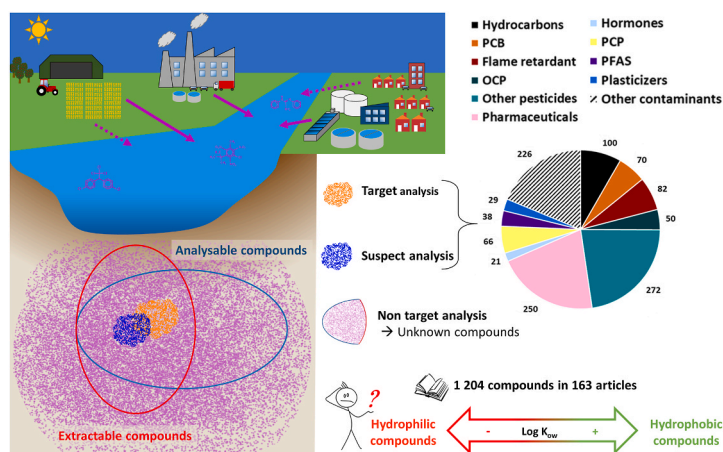
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HIGHLIGHTS

- Continental sediments store a wide array of organic contaminants.
- Even highly hydrophilic compounds have been detected at high concentrations.
- LC-HRMS is the method of choice to explore contaminants of emerging concerns.
- Non-target analysis can help gain deeper knowledge of aquatic contaminants.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling editor: J. de Boer

Keywords:

Suspended particulate matter
Aquatic environment
Emerging contaminants
Sediment contaminants database
Mass spectrometry
Non-target analysis

ABSTRACT

Various industries produce a myriad of synthetic molecules used to satisfy our needs, but all these molecules are likely to reach aquatic environments. The number of organic contaminants found in rivers and lakes continues to rise, and part of this contamination gets transferred into sediments. Analytical methods to detect problematic substances in the environment often use mass spectrometry coupled with chromatography. Here we reviewed a set of 163 articles and compiled the relevant information into a comprehensive database for analysing organic contaminants in continental sediments including suspended particulate matter and surface and bottom sediments in lakes, rivers and estuaries. We found 1204 compounds detected at least once in sediments, and classified them into 11 categories, i.e. hydrocarbons, flame retardants, polychlorinated biphenyls (PCB), plasticizers, per- and poly-fluoroalkyl substances (PFAS), organochlorines (OCP) and other pesticides, pharmaceuticals, hormones, personal care products (PCP), and other contaminants. Concentrations of these compounds varied from a few ng to several mg/kg of dry sediment. Even hydrophilic compounds were detected in high concentrations. Well-known hydrophobic and persistent contaminants tend to be analysed with mass spectrometry coupled to gas chromatography (GC-MS) whereas contaminants of emerging concern (CEC) are usually analysed with liquid chromatography–mass spectrometry (LC-MS). Suspect screening and non-target analysis (NTA), which use high-

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<https://doi.org/10.1016/j.chemosphere.2024.143275>

Received 18 June 2024; Received in revised form 31 August 2024; Accepted 4 September 2024

Available online 12 September 2024

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resolution mass spectrometry, are still scarcely used on sediment but hold promise for gaining deeper knowledge of organic contamination in aquatic environments.

Glossary of abbreviations:

| | |
|---------------------|---|
| APCI | atmospheric-pressure chemical ionisation |
| ASE | accelerated solvent extraction |
| BPA | bisphenol A |
| BSTFA | N,O-bis(trimethylsilyl)trifluoroacetamide |
| CEC | contaminants of emerging concern |
| DDD | dichlorodiphenyldichloroethane |
| DDE | dichlorodiphenyldichloroethylene |
| DDT | dichlorodiphenyltrichloroethane |
| DEET | N,N-diethyl-3-methylbenzamide |
| ECNI | electron capture negative ionisation |
| EI | electronic impact ionisation |
| ESI | electrospray ionisation |
| GC | gas chromatography |
| HBCD | hexabromocyclododecane |
| HCA | hierarchical cluster analysis |
| HCH | hexachlorocyclohexane |
| HRMS | high-resolution mass spectrometry |
| LAB | linear alkyl benzene |
| LC | liquid chromatography |
| Log K _{ow} | octanol/water partition coefficient |
| MAE | microwave-assisted extraction |

| | |
|----------|--|
| MS | mass Spectrometry |
| MTBSTFA | N-tert-butyltrimethylsilyl-N-methyltrifluoroacetamide |
| NSAID | nonsteroidal anti-inflammatory drug |
| NSOBC | natural and synthetic organobromine compounds |
| NSOIC | natural and synthetic organoiodine compounds |
| NTA | non-target analysis |
| OCP | organochlorine pesticide |
| PAH | polycyclic aromatic hydrocarbon |
| PBDE | polybromodiphenyl ether |
| PCB | polychlorinated biphenyl |
| PCP | personal care product |
| PFAS | per- and polyfluoroalkyl substances |
| PFOA | perfluorooctanoic acid |
| PFOS | perfluorooctanesulfonic acid |
| QuEChERS | Quick, Easy, Cheap, Effective, Rugged, and Safe (method) |
| QTOF | Quadrupole time of flight |
| (d)SPE | (dispersive) solid-phase extraction |
| SPM | suspended particulate matter |
| TBBPA | tetrabromobisphenol A |
| UAE | ultrasound-assisted extraction |
| US EPA | United States environmental protection agency |
| WWTP | wastewater treatment plant |

1. Introduction

A recent study estimates that worldwide, over 350000 synthetic organic chemicals with diverse physical-chemical and biological properties have been registered for production and use (Wang et al., 2020) to meet the needs of modern society, regarding public health, food preservation, plant protection, general safety, and way of life. Many of these chemicals and their metabolites are likely to end up in river waters through multiple entry routes including domestic and industrial wastewater discharges and urban and agricultural runoff. Currently, new substances are regularly detected in the aqueous phase and their number continues to grow. (Richardson and Ternes, 2022). Some of them, such as the insect repellent N-N-diethyl-3-methylbenzamid (DEET) (Merel and Snyder, 2016) or more generally organochlorine pesticides (OCP) and polychlorinated biphenyls (PCB), have become ubiquitous around the world and appear in every compartment of the aquatic environment, including water, sediment, and biota (Zaynab et al., 2021). This kind of chemical pollution represents the 5th planetary boundary (out of 9) that has been crossed (Persson et al., 2022). Some classes of organic contaminants have already been associated with major public health issues such as endocrine disruption (Windsor et al., 2019), but co-occurrences of contaminants may have a "cocktail effect", leading to unpredictable global toxicity González-Gaya et al., (2021). Organic contamination therefore demands frequent and exhaustive monitoring campaigns to highlight problematic substances before they trigger new chemical health and environmental crises, such as dichlorodiphenyltrichloroethane (DTT), PCB, or more recently per- and poly-fluoroalkyl substances (PFAS) (Arp et al., 2023).

The detection of trace organic contaminants in aqueous environments usually relies on chromatographic separation coupled with mass spectrometry. Conventional target analysis using low-resolution tandem mass spectrometry enables reliable detection and quantification of a given set of contaminants. However, these techniques require relatively

expensive analytical standards, which often places limitations on the number of compounds monitored. Over the last two decades, high-resolution mass spectrometry (HRMS) has gained in sensitivity and affordability for environmental studies, and is now gaining ground as a complementary method that is expected to facilitate the detection of a greater number of emerging contaminants (Krauss et al., 2010; Hollender et al., 2023). Indeed, non-target analysis (NTA) can detect all the organic chemicals present in a sample, as long as they are ionised in the mass spectrometer source and their concentration is high enough. Each chemical detected by NTA is initially an unknown compound characterised by an accurate mass, a retention time, and some product ions. Suspect screening can then identify some of these unknown compounds without needing standards but using databases. NTA and suspect screening can be associated with target analysis for a more holistic environmental contamination assessment and to screen a broad range of contaminants (Hollender et al., 2017; Escher et al., 2020).

These analytical approaches are commonly used to assess contaminants in water. However, in aquatic environments, contaminants are distributed between water and suspended particulate matter (SPM) as well as bottom sediment, in an equilibrium that depends on their chemical properties. Sediments act as a sink for organic contamination, and this contamination can become remobilised during extreme events such as floods and reappears in the water compartment, where it can cause health issues linked to water uses for example (Crawford et al., 2022). Sediment monitoring is therefore necessary for environmental and health issue. Moreover, the sediment matrix serves as a contaminant archive. The vertical abundance profile of contaminants in a sediment core reflects aqueous contamination through time (Heim and Schwarzbauer, 2013).

The Water Framework Directive watch lists and priority lists of organic contaminants to monitor in river sediments mainly focus on substances with a Log K_{ow} > 5, as they predominantly accumulate in the solid phase rather than in the liquid phase (Gomez Cortes et al., 2020). Studies on sediments commonly report chemicals such as

polybromodiphenyl ethers (PBDE) (Wu et al., 2019), PCB (Wolska et al., 2014) or polycyclic aromatic hydrocarbons (PAH) (Maletić et al., 2019), all of which are qualified as persistent organic pollutants (POP). Due to their persistency, toxicity and ubiquity, some of these POP are also listed in the Stockholm convention for regulation (Secretariat of the Stockholm Convention, "<https://www.pops.int/TheConvention/ThePOPs/AllPOPs>"). However, little is known about other organic contaminants of emerging concern (CEC) in sediments. And yet, Chiaia-Hernández et al. (2020a) detected 69 CEC in sediment, some of which have Log K_{ow} below 2.

To the best of our knowledge, there has not been a comprehensive review of contamination in continental sediments since Parkinson and Dust (2010) and Heim and Schwarzbauer (2013). Parkinson and Dust (2010) published a state of the art on inorganic and organic contamination in sediments that addressed POP (PCB, PBDE ...) and CEC. They focused on trends in analytical methods from sampling to analysis, including sample preparation, in order to identify past and future advances for organic and inorganic contaminant detection in the environment. Their review was done at a time when the main extraction and analysis techniques were Soxhlet solvent-extraction and gas or liquid chromatography coupled with low-resolution MS. They signalled the rise of new methods such as pressurised liquid extraction and HRMS to detect the emerging POP of the time. However, since 2010, knowledge on CEC in the environment has grown and analytical strategies have evolved. Heim and Schwarzbauer (2013) reviewed historical pollution records and dating in sediment cores.

The primary objective of this review is to highlight the broad variety and concentration ranges of CEC already detected in continental sediments. The second objective is to provide an overview of the analytical approaches applied according to class of contaminants. Finally, these approaches will be discussed, regarding the number of screened compounds and instruments needed, in order to highlight research needs.

2. Methodology

2.1. Selection of scientific papers

Articles were searched from the Web of Science (WoS) "core collection" platform. We focused on articles dealing with surface sediments and sediment cores from continental surface waters. We chose to also consider suspended particulate matter (SPM), as it represents the particulate phase before sedimentation. To cover the widest possible range of relevant contaminants, the keywords on contaminants came from the NORMAN SusDat database compiling more than 100 000 compounds of interest for water contamination (Mohammed Taha et al., 2022; "<https://www.norman-network.com/nds/susdat/>"). The final set of titles of categories and sub-categories of compounds constituted a list of 108 keywords, which were introduced in the search equation.

We did not consider papers published before 2010 (i.e. before the review by Parkinson and Dust, 2010) nor papers on inorganic contaminants. Details of the search equation can be found in Supplementary material S1 – 1 and 2 (S1 – 1 and S1 – 2). On April 12th, 2023 on WoS, our search equation screened out 660 articles.

To refine and finalise our selection, a manual sorting was done to remove studies on soil, dust or sewage sludge. Finally, articles that did not use mass spectrometry (low or high resolution) for contaminant detection, were also removed. After this manual sorting, 163 articles remained, as listed in S1 - 3.

2.2. Description of the database

Articles were examined from two angles. First, we gathered information on the methodologies used to characterize sediment contamination: sampling method (site, number of samples, kind of samples), drying, storage, solvent extraction (technology, solvent, etc.), purification, and analysis (chromatography, ionisation, and mass spectrometry).

Second, we listed the identity of the contaminants measured and their concentrations. Maximum and minimum concentrations were referenced for every contaminant when available. We used the R package "Chemweb" to homogenize contaminant names and chemical characteristics by looking for InChI key and finding characteristics on PubChem. We assigned the PubChem CID for each contaminant to facilitate data management. Each chemical was assigned to a group: pharmaceuticals and drugs, personal care products (PCP), hormones, organochlorine pesticides, other pesticides, PFAS, hydrocarbons, PCB, flame retardants, plasticizers, and other contaminants. A subcategory was assigned for each pharmaceutical using the DrugBank website (Knox et al., 2024). We also assigned each pesticide to a structure-related subcategory, using the British Crop Production Council website ("<http://www.bcppesticidecompendium.org>").

The database including relevant information retrieved from the set of articles is available in Supplementary material 2 (S2): S2 – Table 1 (179 lines) gathers information on articles reviewed, studied samples and the analytical methods; S2 – Table 2 (2911 lines) gathers concentrations measured for each contaminant; S2 – Table 3 (1261 lines) lists details on the classification of the contaminants and their physico-chemical properties taken from PubChem.

3. Results and discussion

3.1. A majority of the 163 selected papers focus on river surface sediment

Almost two thirds of the papers deal with sediments collected in Europe or Asia. China is the most represented country with 38 papers out of the 163 selected. Region like South America, Africa or Oceania are vastly underrepresented (Fig. 1A).

Continental waters are split into three types of aquatic environments: rivers, lakes and coastal areas under the influence of the sea such as estuaries or coastal wetlands (Fig. 1B). A large majority of the papers selected (112 out of 163) investigate contaminants in rivers.

As mentioned in part 2.1, we considered SPM in the water column, surface sediments and core sediments. A majority of papers dealt with surface sediment (128 out of 163), probably because they are easier to sample (Fig. 1C). Indeed, sediment cores need a corer (not easily available) whereas SPM can be sampled with a particle trap or in situ centrifugation or by filtering of huge volume of water. In summary, the majority of the selected studies investigate surface sediments in rivers.

3.2. Diversity and wide concentration range of organic contaminants in sediments

Across the 163 studies, a total of 1204 contaminants were found in sediments at least once (S2 – Table 3). These contaminants were distributed across 11 categories as presented in Fig. 2A. Almost half of these contaminants (46%) were classified as pharmaceuticals or pesticides. These two groups also encompassed a huge diversity of compounds. Pharmaceuticals included several subcategories such as antibiotics (Luo et al., 2011; Radović et al., 2015; Tong et al., 2017), antidepressants (Golovko et al., 2020), opioids and betablockers (Ramil et al., 2010). Pesticides included herbicides, insecticides and fungicides. OCP were separated from other pesticides because they are well-known (a long history of frequent monitoring in waters) since being listed under the Stockholm convention. Among the 11 categories, 7 categories can be classified as CEC: pharmaceuticals, other pesticides, PCP, hormones, PFAS, plasticizers, and other contaminants. Within these CEC, some contaminants (like pesticides) were only recently found in the environment due to recent uses and releases. Other CEC, such as PFAS, have long been present in the environment, but discussion about them has only recently emerged. Even though PCB have been used as flame retardants, they were kept as a separate category because of their various other uses and their specific focal role in health and environmental concerns.

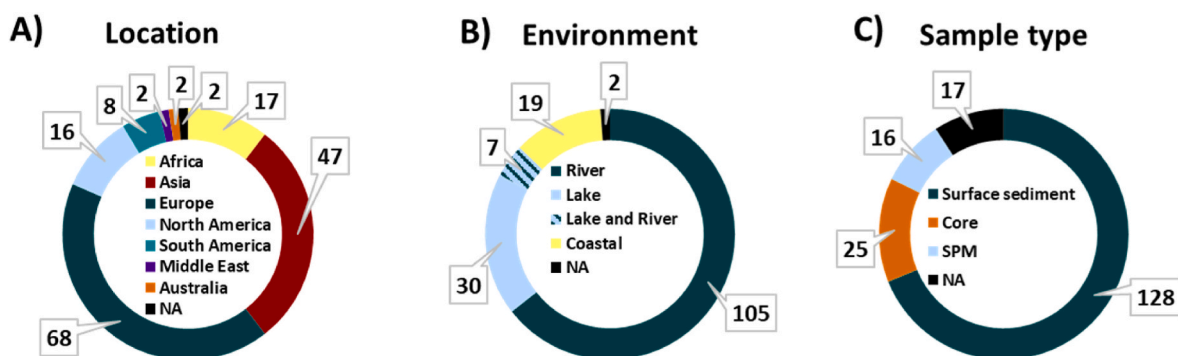


Fig. 1. Number of sediments studied per A) location, B) aquatic environment, and C) sample type across the 163 reviewed articles.

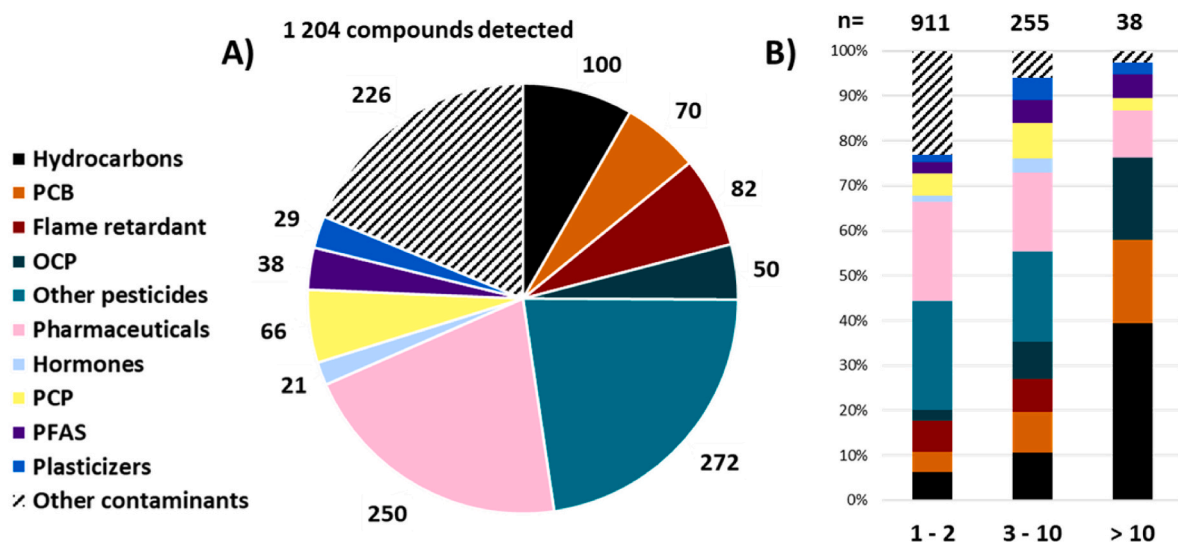


Fig. 2. The 11 categories of contaminants and number of contaminants detected in sediments A) per category and B) per number of papers investigating them.

3.2.1. Diverse patterns of sediment contamination

3.2.1.1. The well-known contaminants. Each non-CEC category count several dozen contaminants (from 50 to 100), and several of them were studied in more than 10 papers. OCP comprised 50 compounds, but some of them are different isomeric forms of a same compound, and so the OCP group only counts 30 compounds with different chemical formulae. Isomeric forms of hexachlorocyclohexane (HCH), including lindane (gamma-HCH), and DDT with its metabolites dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE), were measured in more than 10 studies. OCP were used for their insecticidal effect, and they were banned in most developed countries due to their persistency and high toxicity. Hydrocarbons comprise synthetic compounds such as linear alkyl benzenes (LAB), but also compounds produced naturally, such as some alkane and alkenes, terpenes, and some PAH. PAH are still mainly non-purposely produced by human activities, typically through burning wood, fossil fuel, or biofuel. PAH monitoring focus on 16 compounds (listed by the United States Environmental Protection Agency (US EPA)), but more than 50 PAH are referenced in our database. Concerning PCB, studies usually monitor the 7 PCB indicators (PCB 28, 52, 101, 118, 138, 153, and 180) and the 12 dioxin-like PCB. Of the theoretical total of 209 PCB congeners, 70 congeners were measured in sediments. A few studies measured between 39 and 50 PCB (Škrbić et al., 2018; Ierhievie et al., 2020; Iwegbue et al., 2020, 2022).

Flame retardants (other than PCB) includes chlorinated, brominated and organophosphate compounds. A first subcategory of flame retardant

is composed of 28 PBDE congeners, of which PBDE-47, 99, 153, 100 and 209 are the most frequently analysed. PBDE were used to replace PCB, before being replaced by other flame retardants, such as organophosphate flame retardants (Zha et al., 2018). Among the 20 organophosphate flame retardants referenced in our database, triethyl and tributyl phosphate are the most analysed in sediments. More recently, tetrabromobisphenol A (TBBPA) (Liu et al., 2019) and hexabromocyclododecane (HBCD) (Xu et al., 2013; Zhu et al., 2013) have also been used as flame retardants. Both have been found in sediment and can be considered as emerging contaminants.

3.2.1.2. Contaminants of emerging concern. In our database, almost 97% of the contaminants are measured in sediments in less than 10 studies if not 1 (Fig. 2B). These contaminants can be classified as CEC due to their recent interest and/or the lack of knowledge on their occurrence in aquatic environments. They are represented by 7 categories: PFAS, other pesticides, pharmaceuticals, PCP, hormones, plasticizers, and other contaminants. All show wide diversity through several subcategories (S1 - 4).

Concerning PFAS, some of them, like perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are already well known and included in the Stockholm convention. Nevertheless, in the context of current discussion about PFAS-related health concerns in Europe, the scientific community has warned that thousands of unknown and potentially toxic PFAS are likely to be present in aquatic environments, and that there is a serious lack of knowledge about the extent of this contamination. PFAS are therefore considered as CEC. In 2018, the

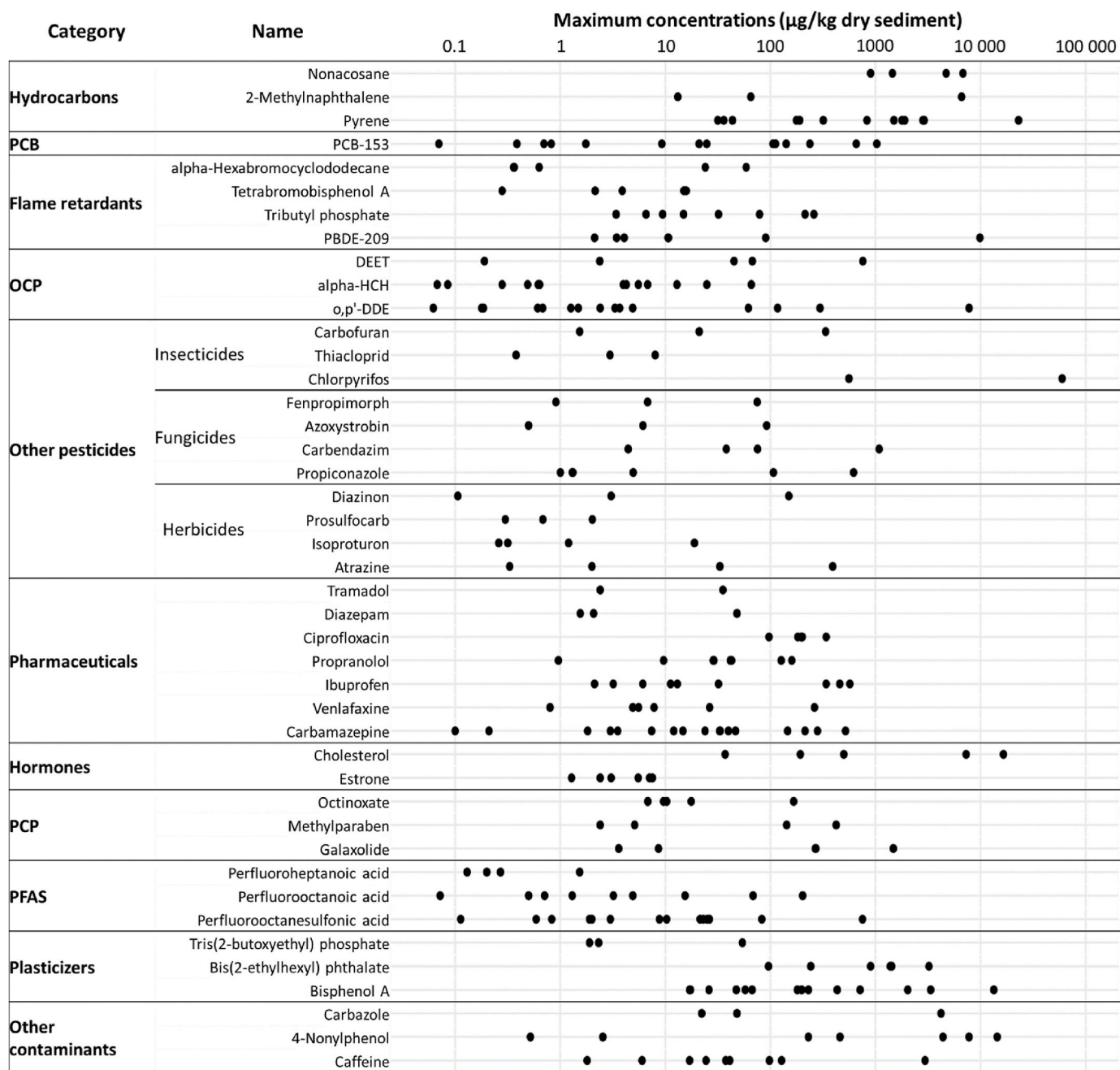


Fig. 3. Maximum concentrations measured per article for the most detected compounds of each categories.

Organisation for Economic Co-operation and Development identified 4730 PFAS-related CAS numbers. Our database referenced 38 PFAS, 3 of which (PFOS, PFOA and perfluorononanoic acid (PFNA)) are documented in more than 10 studies.

Other pesticides can be subcategorized into 3 groups: herbicides, insecticides, and fungicides. Each of these groups can be split into classes based on their chemical structures. Although most of these pesticides are well known, we have classified them as CEC because some of them are currently the subject of controversy, with debate about whether to ban them on the grounds of their proven environmental toxicity. The two main classes of herbicides are triazine herbicides and urea herbicides. Some triazines are still found in aquatic environments although they are banned for a long time in many countries (e.g. atrazine since 2003 in European Union) (Bastos and Haglund, 2012; Müller et al., 2021). Other triazine herbicides, like terbutryn or terbumetron, are still in use (Massei

et al., 2018; Kandie et al., 2020). Some urea herbicides are also well documented, such as isoproturon or diuron, which have been banned in France but not in European Union. Other classes of herbicides have been less investigated, such as N-phenylimide herbicides that is only represented by flumioxazin (Babić et al., 2018) or the aromatic-acid herbicide chloramben that is considered less toxic than other herbicides. Finally, glyphosate is documented in only 3 studies (Babić et al., 2018; Lupi et al., 2015; Machate et al., 2021). Fungicides found in sediments are often azole fungicides, such as difenoconazole which is effective against mildew (Kandie et al., 2020), or propiconazole and tebuconazole which are the most measured in sediments. The main classes of compounds used to replace OCP insecticides are organophosphorus insecticides like chlorpyrifos, malathion or dimethoate (Kandie et al., 2020; Radović et al., 2015) and carbamate insecticides like pirimicarb. Lastly, some pesticides found in sediment are growth regulators, for example

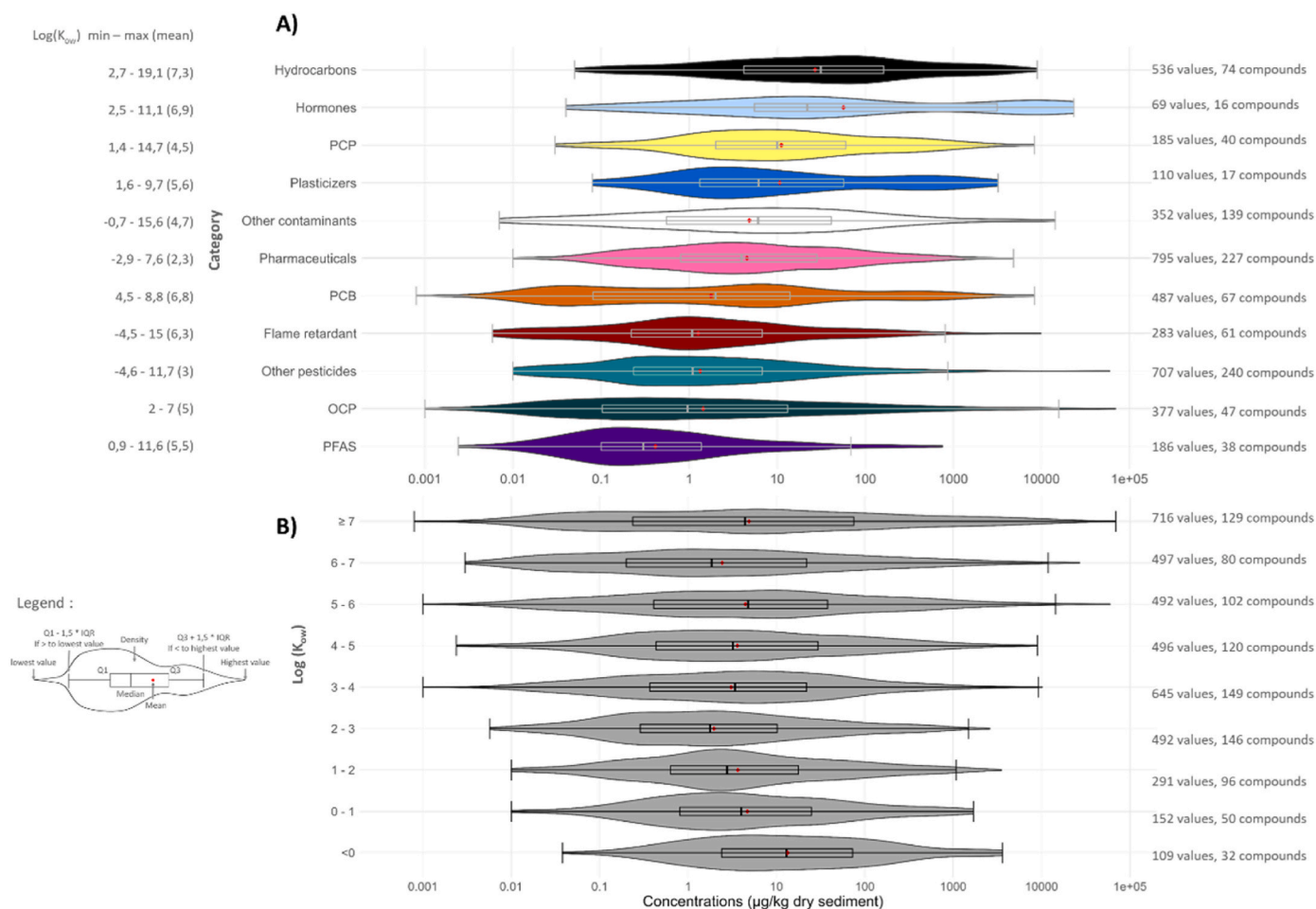


Fig. 4. Concentration ranges measured A) by category of contaminant and B) by Log K_{ow} (B).

thidiazuron or paclobutrazol (Babić et al., 2018). Note that here, the full diversity of pesticides found in sediment cannot be discussed, as our search found 83 different structural classes of pesticides, and in some cases the same molecule can have various applications in use, such as fipronil used as an insecticide for seeds but also to control ticks and fleas on pets or cockroaches in household products.

Pharmaceuticals falls into several subcategories depending on their therapeutic use. Note that there are molecules useable for several therapeutic purposes. In our database, antibiotics such as ofloxacin and erythromycin (Luo et al., 2011) have been detected in sediment, but also anti-parasitic and antifungal drugs such as mebendazole used to treat parasitic worms and fluconazole used to treat parasitic worms or different fungal infections affecting the mouth, lungs, skin, etc. (Massei et al., 2018). In this review, 39 antimicrobial drugs were referenced, covering antibiotic, antifungal and antiparasitic drugs. There are 22 antidepressants, including venlafaxine or vortioxetine (Fernandes et al., 2020; Santos et al., 2016), and 20 anti-psychotic drugs to treat schizophrenia like clozapine (Babić et al., 2018). Some betablockers used to treat heart health issues, such as propranolol, can treat anxiety too (Ramil et al., 2010). Anti-convulsants were also found in sediment, such as carbamazepine. There are also 22 anxiolytics, 8 betablockers and 6 antihypertensive drugs within the 163 articles. Some analgesics (used against pain) were found in sediments, such as the two non-steroidal anti-inflammatory drugs (NSAID) diclofenac and ibuprofen (Chakraborty et al., 2019; Gumbi et al., 2019). Twenty-six stronger opioid analgesics were also detected, including morphine, fentanyl, and codeine (Babić et al., 2018; Gumbi et al., 2019). Other compounds classified as pharmaceuticals included proton pump inhibitors, hormone

receptor antagonists, antiretroviral drugs, and their metabolites. Finally, 16 illicit drugs were found in sediment too, including methamphetamine, cocaine, cannabidiol, and ketamine (Babić et al., 2018; Gumbi et al., 2019). It is hard to get information on consumptive use of these compounds, but sediment records can inform on patterns of social habits. Another example is sildenafil, better known as Viagra, which was found in surface sediment downstream of a wastewater treatment plant (WWTP) serving Bordeaux in France (Aminot et al., 2015).

There are many other pharmaceutical products potentially present but that have not yet been explored in sediments. The public DrugBank database (Knox et al., 2024), which gathers information about drugs, their targets, mechanisms of action, etc., counts around 2000 pharmaceuticals approved in the EU and USA, which is why further sediment investigation is needed to increase knowledge on their nature, concentration levels, and persistence.

Among PCP, most abundant subcategory is fragrances, especially synthetic musk fragrances like galaxolide, tonalide, musk xylene and musk ketone (Lou et al., 2016; Sang et al., 2012). There is less evidence of other fragrances such as versalide (Smital et al., 2013) or diphenyl ether (Duong et al., 2014), which were both found in sediment only once. We also listed 16 UV filters contained in sunscreen creams, such as ethylhexyl-methoxycinnamate, octocrylene, and UV-234 (Kameda et al., 2011; Kaiser et al., 2012; Wu et al., 2020). Some antimicrobials are added to personal care creams for better preservation, such as the widely-used triclosan, identified in 13 papers on sediments. Parabens are used in PCP as antifungal and antibacterial preservatives. Methyl-, ethyl-, propyl-, and butyl-parabens were found in sediments from Albufera Natural Park, showing the extent of this contamination brought

by tourism (Sadutto et al., 2020).

This review counts 21 hormones already detected in sediments. Most of them are natural, such as sterols like coprostanol or cholesterol that can be used as indicators of animal or human life (Lahti and Oikari, 2012). Other natural sterols detected include phytosterols produced by plants, such as stigmastanol and fucosterol (Škrbić et al., 2018). Finally, there are also estrogens, which can be endogenous or used as medication for birth control or menopause therapy. The synthetic estrogen diethylstilbestrol was used between the 1940s and 1980s to prevent miscarriage, but turned out to be a public health problem as it causes sterility in offspring. It was also used as a growth promotor for livestock before it was banned in 1979 in the USA and 1981 in Europe (Mitra and Philip, 2014).

In the plasticizers category, we found additives such as bisphenol A (BPA), one of the most frequently studied in sediments, along with 11 other bisphenol-analogs that have already been detected in sediment, such as dibromobisphenol, bisphenol BP, and bisphenol S (Chamorro et al., 2013; Ye et al., 2021). Sediments also contained UV stabilizers, which are used to protect plastics against light degradation (Lu et al., 2016). Phthalates are also added to plastics to improve their flexibility. Here, 17 different phthalates have already been found in environmental sediments (Chakraborty et al., 2019; Smital et al., 2013). Organophosphate chemicals are used as additives in plastics, textiles, electronics, etc. for their various flame retarding, waterproofing and plasticizing properties. They are found in different environmental matrices and can cause endocrine disruption, lipidome homeostasis disorders, and reproductive failure (Ye et al., 2021).

Compounds gathered in the "other contaminants" category were mainly chemicals used in the formulation of materials. Examples include quaternary ammonium compounds (Li and Brownawell, 2010) used for antiseptic or disinfectant action, phenols used in diverse industrial processes (Yang et al., 2020; Zhou and Broodbank, 2014), and siloxanes used for polymers (Krogseth et al., 2017; Lee et al., 2019). Some chemicals are not synthesised purposely but are by-products of thermal processes, such as dioxins/furans (Gao et al., 2015a) and polyhalogenated carbazoles (Wu et al., 2017; Li et al., 2022). To finish, the most analysed chemical in this category is caffeine that can be used as a marker of anthropic pressure as it ends up in the environment through treated wastewater.

3.2.2. Concentration levels according to nature of the contaminant

Unless otherwise stated, all concentrations given here are relative to dry weight of sediment and are detailed in S2 – Table 2. There is a wide range of concentration levels between contaminants and between sites, from a few ng/kg up to 10 mg/kg. For instance, Peng et al. (2017) found triclocarban at concentrations from 1.82 to 3440 µg/kg in different sediments near Guangzhou city (China). Fig. 3 shows maximum concentrations in each studies measuring the most referenced compounds of each subcategory. Non-CEC compounds, such as PBDE-209 or hydrocarbons, reached high concentrations. For example, the PAH fluoranthene was found at up to 22000 µg/kg in an industrial area of northern Sweden in 2012 (Bastos and Haglund, 2012), and the flame retardant PBDE-209, which does not generally exceed 90 µg/kg, reached 9862 µg/kg in SPM in Songhua river, China (Wang et al., 2015). Nevertheless, some CEC also reached concentration above 1 mg/kg, such as chlorpyrifos (Duong et al., 2014) and carbendazim (Diamanti et al., 2020) (Fig. 3). Plasticizers, especially bisphenols and multi-purpose industrial ("others" category) were also found at high concentrations (up to 13000 µg/kg for BPA) in sediments from Sihwa lake in Korea, close to a tidal barrage (Liao et al., 2012).

Fig. 4A charts minimum and maximum concentrations of the most detected compounds per category. PCB and OCP had the largest concentration range. PCB are often reported as the sum of concentrations of several congeners, and can thus reach high concentration levels, such as the 7 PCB indicators that reached 4930 µg/kg in sediment from Escravos river basin in Nigeria (Iwegbue et al., 2020). Among hormones, there are

significant differences between estrogens and sterols. Estrone did not exceed 8 µg/kg, whereas coprostanol and cholesterol were detected at over 10000 µg/kg. Synthetic hormones include, Ethinyl-estradiol, an estrogenic medication in birth control pills, found at 17 µg/kg. Diethylstilbestrol, the synthetic hormone already mentioned, was found at 20 µg/kg in the Songhua river, China (Zhang et al., 2014).

Studies often examine the physical-chemical properties of contaminants, and especially their Log K_{ow} , to explain their concentration levels in sediments. As low Log K_{ow} compounds have a high affinity with water, we expected them to be undetectable (or detectable only at low concentrations) in sediment. Fig. 4B presents concentration ranges by Log K_{ow} . It shows that the concentration level of a contaminant in sediment is not related to its Log K_{ow} . Indeed, sediments contained high concentrations even of hydrophilic compounds (e.g. up to 1500 µg/kg for the antibiotic ofloxacin, with Log K_{ow} = -0.4 (Yang et al., 2010)). High sediment concentrations of a molecule can be explained by the tonnage produced and discharged and its persistence in the environment. This is why studies need to explore hydrophilic molecules in sediments, unlike the usual practice, as there is a lack of knowledge in this area.

The highest levels of contamination are easily explained by human activities surrounding the sediment location. As an example, Kucher and Schwarzbauer (2017) analysed sediment cores from the coast of California downstream of a chemical corporation that had released approximately 1500 to 2000 tons of DDT up until 1971. They found p, p'DDE at 69000 µg/kg at 38 cm depth in a core sampled in 2003. PCB were measured with the highest concentrations in Nigeria near industrial activities, especially petroleum, at 4930 µg/kg for the sum of the 7 PCB indicators in surface sediments (Iwegbue et al., 2020). The highest levels of hydrocarbons, phthalates and pesticides were found by Bastos et al. (2012) in sediments from an industrial area of northern Sweden known for production of paper, pesticides, bulk chemicals and chlor-alkali, with levels of chrysene up to 4900 µg/kg, diphenylamine up to 220 µg/kg, and diethyl phthalate up to 43000 µg/kg. The highest levels of pharmaceuticals were found downstream of the city of Zagreb and were explained by urban activities (and human density) (Babić et al., 2018). Lack of wastewater treatment can also explain high concentrations. De Sousa et al. (2018) detected the PCP triclosan at 9171 µg/kg in SPM and 903 µg/kg in surface sediment of Jundiáí river in Brazil, a river receiving domestic and industrial untreated wastewaters as well as waters from a WWTP.

Based on the papers selected, substance concentrations per category were roughly the same between Europe and Asia (S1 - 5). It is difficult to compare between other regions due to the imbalance in the amount of data available. Global concentrations are higher in sediment from rivers compared to lakes (S1 - 6).

3.2.3. Contamination in SPM vs surface sediments vs sediment cores

Some authors have analysed a set of compounds in both SPM and surface sediments. (Zhang et al., 2018; Zha et al., 2018; Aminot et al., 2015; De Sousa et al., 2018; Montuori et al., 2014; Mudumbi et al., 2014; Rivetti et al., 2015). Concentrations of some organophosphate flame retardants are sometimes higher in sediment vs SPM (Zha et al., 2018) but sometimes lower (Zhang et al., 2018). All pharmaceuticals and hormones detected in both surface sediment and SPM show higher concentrations in SPM: more than 10 times higher for neflinavir, meprobamate and bisoprolol according to Aminot et al. (2015) and more than 100 times higher for estrone and diclofenac according to De Sousa et al. (2018). De Sousa et al. (2018) assumed that the higher concentrations is due largely to the higher fine-grained fraction of SPM but also partly to flow conditions, which can delay sedimentation and slow the process of contaminants settling into river surface sediment. These results also raise the issue of compound stability, as some compounds could be degraded before settling in the riverbed.

Conversely, higher concentration levels in surface sediments than SPM were found for hydrophobic compounds, such as PCB in Montuori

et al. (2014) or PFOA and PFOS in Mudumbi et al. (2014).

Rivetti et al. (2015) were able to detect okadaic acid and anatoxin-a only in SPM and not in sediments. They detected okadaic acid during a bloom of dinoflagellates that produce the compound in water, with too little time for it to accumulate in sediments. Anatoxin-a contamination could be caused by remobilisation during a flood of surface sediment where the cyanobacteria producing anatoxin-a live.

Studies on sediment cores can serve to assess temporal trends in contamination. To do so, cores need to be sub-sampled vertically. Depending on the contaminant, its concentration in sediment can decrease or increase with depth and time. To illustrate, Kucher and Schwarzbauer (2017) showed a reduction of DDT and its metabolites with depth over a period running from 1971 to 1993 and then stagnation until 2003. Mourier et al. (2018) observed a rapid reduction of PCB in the mid-1980s, which is logically explained by the ban on PCB in 1987 in France. PCB concentrations are still decreasing, but at a slower rate since the 2000s. He et al. (2020) observed a degradation of DDT with depth of sediment cores from Meijiang river basin in China, but they detected the presence of HCH in the top sediment layer, which testifies to recent use. He et al. (2020) explained this presence of HCH by the recent establishment of a new industrial park.

Concentrations of other compounds were shown to decrease with time (*i.e.* concentration increase with sediment depth), such as PAH and PBDE in Poyang lake in China (Wan et al., 2020), organophosphate in Taihu lake in China (Ye et al., 2021), or the antidepressant citalopram in a lakes from central Finland (Lahti and Oikari, 2012). Liao et al. (2012) highlighted a replacement of BPA by BPS since 2001 due to the inversely correlated concentrations of these two plasticizers. Hagemann et al. (2019) traced sources of organic contamination in aquatic environments, and attributed some compounds to industrial sources (e.g. PCB, di-iso-propylnaphthalenes and dichloroanilines) but others to domestic sources (e.g. PCP, LAB, and human faecal steroid cholesterol). Lupi et al. (2015) compared concentrations of glyphosate and its degradation product AMPA in a sediment core and the stream water of Quequén Grande river in a region of Argentina producing soybean. As concentrations were under limit of quantification in water but ranged from 2 to 14 µg/kg in sediments, they infer that sediment acts as a sink for this hydrophilic pesticide.

Cores from lake Greifensee and lake Lugano in Switzerland have been the subject of several studies (Chiaia-Hernández et al., 2017, 2020a, 2013) looking at anthropogenic chemical pressure on aquatic environments and highlighting input trends based on concentrations of several organic contaminants. For example, Chiaia-Hernández et al. (2013) detected peak input of quaternary ammonium compounds in the 1970s and the beginning of triclocarban contamination in the 1960s. In another study, Chiaia-Hernández et al. (2020b) observed an increase of the pesticides irgarol, terbutryn, and prometryn from the 1990s until the day preceding the sampling (2012) and the apparition of other pesticides propiconazole, fludioxonil, DEET and acetochlor in the preceding decade (2002–2012). Chiaia-Hernández et al. (2017) also used hierarchical clustering analysis to highlight groups of contaminants evolving the same way, distinguishing compounds affected by construction or upgrading of a WWTP close to sampling point.

3.3. Methodologies used to characterize sediment contaminations

3.3.1. Sampling and pre-treatment

All analytical methods are detailed in S2 – Table 1. The majority of surface sediments are collected using a simple stainless shovel, which is the easiest way to collect samples for grab sampling. There are other specific tools available for grab-sampling surface sediment, such as the Van Veen grab (Ohoro et al., 2021) or Ekman sampler (Agunbiade and Moodley, 2016). Coring is performed to sample bottom sediments and explore former contaminations. Corers are designed to take deeper samples and preserve the order of the sediment layers that can then be related to periods of time. The core can be then divided into thinner

layers of sediment to study shorter periods of time (Mourier et al., 2014). However, some authors sampled cores but pooled them (Lübeck et al., 2020; Yang et al., 2015) to give a sample integrating contamination over a long period of time (depending on core depth and sedimentation rate).

SPM can be sampled using sedimentation boxes (Rüdel et al., 2013; Masson et al., 2018) or by filtration (Müller et al., 2021; Yang et al., 2020) or centrifugation (Loos et al., 2017) of a large water volume. Sedimentation boxes are left in the river for several days or weeks, which make them a time-integrating tool. Filtration and centrifugation enable sampling of both water and SPM to assess the total flux of contamination driven by the river.

Before analysis, sediments need to be homogenised, sieved and, in most cases, dried. Sediment can be freeze-dried or air-dried. In the literature, air-drying is done at a large range of temperatures, from room temperature up to 105 °C, depending on the thermo-lability of the compounds studied. A huge majority of authors work on dry sediments, but a few have analysed wet sediment (Tan et al., 2018; Duong et al., 2014). Duong et al. (2014) detected 189 contaminants in sediments from 16 rivers across Vietnam, and then calculated the amount of moisture in the sediment to provide the concentration in µg/kg of dry sediment as well.

When samples are stored prior to analysis, it is generally at around –20 °C, but some laboratories keep them at 4 °C or even at room temperature. Few samples were archived at ultra-low temperature, *i.e.* at –80 °C (Kameda et al., 2011; Ye et al., 2021) or even –150 °C (Rüdel et al., 2013). As an example, the Environmental Specimen Bank (Chaplow et al., 2021) held samples from coastal and freshwater environments stored at –150 °C. There has been no information reported on the stability of the contaminants during the storage period, even for long periods of times.

3.3.2. Extraction of contaminants from the sediment samples

As shown in Fig. 5, acetone, hexane and dichloromethane are the solvents most used before GC-MS, whereas methanol and water are the solvents most used for LC-MS. Methanol can be used to extract the least hydrophobic compounds before a GC-MS analysis, and acetone or acetonitrile are suitable for the least hydrophilic compounds before LC-MS. Acidification is often done by adding 1% formic acid (Massei et al., 2018; Brand et al., 2018; Mudumbi et al., 2014) or acetic acid (Gamhewage et al., 2019; Paíga and Delerue-Matos, 2016; Mudumbi et al., 2014) and buffer solutions. Acidification changes the polarity of a compound to make it more extractable. Extraction can be done with various mixtures of solvents and/or successive extractions with different solvents (two, three or four successive extractions for accelerated solvent extraction (ASE) and ultrasound-assisted extraction (UAE)).

Extraction can be done at different temperature and pressure conditions according to the technique employed. Soxhlet, microwave-assisted extraction (MAE) and ASE are usually performed at high temperature, with a maximum at 160 °C, 150 °C and 170 °C, respectively, for 12 organophosphate flame retardants (Zhang et al., 2018), HBCD, and bisphenol AF (Zhao et al., 2017b). In addition, compared to Soxhlet and MAE, the ASE technique combines both high temperatures and high pressures.

UAE can work at temperatures up to 60 °C (e.g. Liao et al. (2012) for 15 PFAS), but is usually performed between room temperature and 40 °C. Other types of extractions at room temperature consist of shaking or stirring the solvent in contact with the sample. Among them, the QuEChERS method (Quick, Easy, Cheap, Effective, Rugged and Safe) was designed to be cheap and easy to implement and can combine extraction using solvent and purification salts using powdered adsorbent (dispersive solid-phase extraction) (e.g. Santos et al. (2016) for 9 pharmaceuticals). QuEChERS was historically used to target pesticides in food but has now found a broader range of applications.

UAE and ASE are by far the most popular techniques for extractions from sediments (Fig. 5), and are both used before LC-MS and GC-MS analysis. We counted more studies using UAE than ASE (70 vs 52),

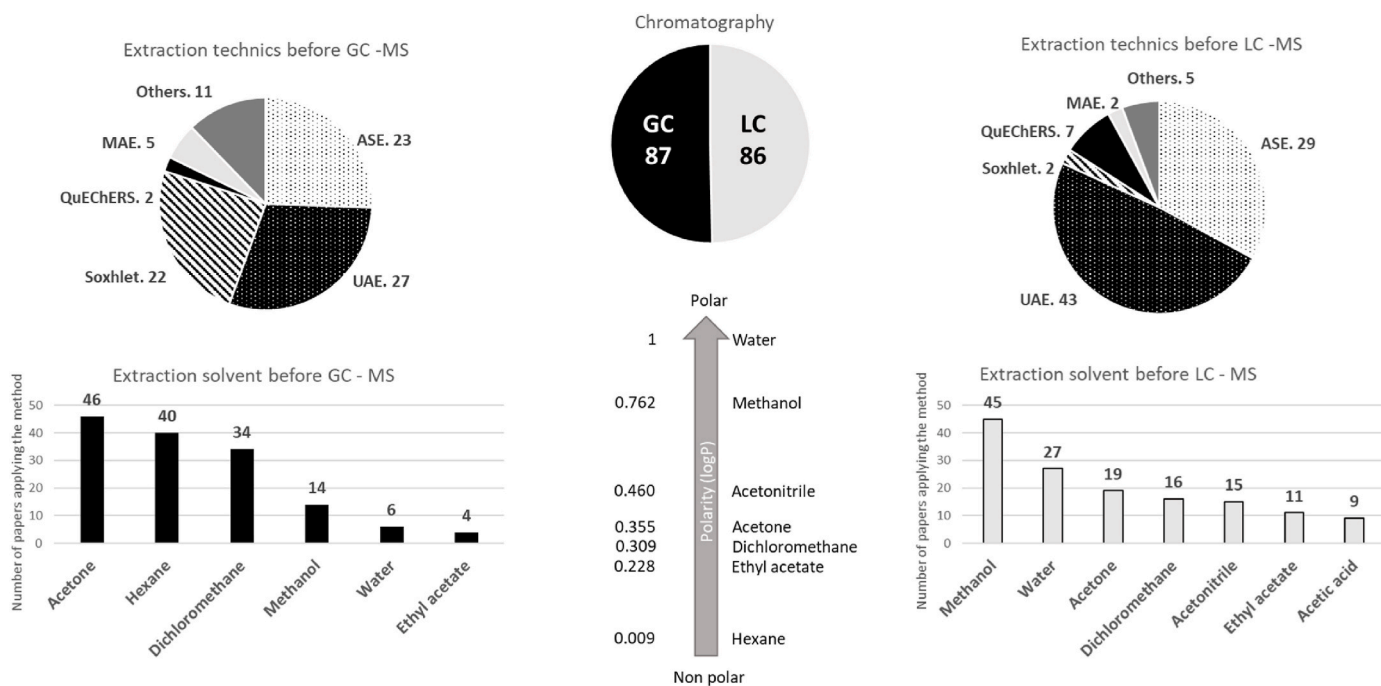


Fig. 5. Extraction techniques and solvents used for chromatographic analysis.

probably because UAE is more affordable and easier to use than ASE. Soxhlet is also widely used, but only for the most hydrophobic compounds analysed by GC-MS, i.e. OCP (Tombesi et al., 2018; He et al., 2020; Ivanova et al., 2021), PCB (Gakuba et al., 2015; Iwegbue et al., 2020, 2022), organophosphate flame retardants (Zhang et al., 2018), brominated flame retardants (Wang et al., 2015), and hydrocarbons (Kanzari et al., 2012, 2014; Lu et al., 2012). This can be explained by the widely-used US EPA methods 3540 and 1694 that advises Soxhlet extraction for such compounds. The other extraction techniques, such as MAE (Chakraborty et al., 2019; Kotnik et al., 2014; Mekonnen et al., 2015), QuEChERS (Nannou et al., 2019; Nejumal et al., 2018; Mondal et al., 2018) or shaking (Lima Do Rêgo et al., 2021; Esparza et al., 2011; Liao et al., 2012) are less popular but can nevertheless be used for a wide variety of contaminants. Note that high temperature can affect thermo-labile compounds or lead to the loss of volatile compounds, which is why toxins like digitoxin (Babić et al., 2018), okadaic acid and anatoxin-a (Rivetti et al., 2015) were extracted with UAE.

The combination of the mass of sediment and the volume of extraction solvent before chromatographic analysis determines the limits of detection and quantification. The extracts can be diluted to modulate matrix effects and reduce LC or GC-MS interferences, but overdilution can risk failing to detect the compounds present in the lowest concentrations. Authors often use a mass of between 0.1 g and 10 g of sediment, but some go higher, such as Gakuba et al. (2015) who used 60 g of sediment for a Soxhlet extraction with a large solvent volume (300 mL before evaporation). The mass ratio of dry sediment to volume of solvent before injection (g/mL) varies between 0.02 and 100 (Khuman et al., 2020; Brand et al., 2018). The mass of sediment or final volume of the extract is not related to the extraction technique. However, in the papers reviewed here, a low mass of sediment (1 g and lower) often corresponds to LC analysis whereas high mass (10 g or more) often corresponds to GC analysis.

In the huge majority of studies, a purification step is applied after or during the extraction. Purification is achieved using gel permeation chromatography (Mourier et al., 2014; Ololade, 2014; Rivetti et al., 2015) or adsorption chromatography. The sediment extract goes through a solid phase made of silica, SiO₂ and/or alumina, Al₂O₃, or Florisil composed of magnesium. These solid phases should retain

undesirable compounds in the matrix that can cause interference in the analysis. Primary and secondary amines are also used to remove organic and fatty acids, sugars and anthocyanins (Nannou et al., 2019; Vulliet et al., 2014; Kuzukiran et al., 2016; Ye et al., 2021). Purification is mainly done in cartridges (solid phase extraction (SPE)) (Yang et al., 2010; De Sousa et al., 2015; Agunbiade and Moodley, 2016; Kotnik et al., 2014) and rarely in chromatographic columns (Irerhievie et al., 2020; Ivanova et al., 2021; Iwegbue et al., 2020). The phase can also be directly mixed with the sample and solvent during extraction (dispersive SPE) (Chiaia-Hernández et al., 2020a; Yuan et al., 2018; Masiá et al., 2015), as is the case when using QuEChERS.

Prior to GC-MS, activated copper can be used to remove sulphur compounds (Kucher and Schwarzbauer, 2017; Škrbić et al., 2018; Kanzari et al., 2012, 2014). Sodium sulphate (Na₂SO₄) (Lübeck et al., 2020; Kucher and Schwarzbauer, 2017; Chamorro et al., 2013; Gakuba et al., 2015; He et al., 2020) or magnesium sulphate (MgSO₄) (Nannou et al., 2019; Fernandes et al., 2020; Santos et al., 2016; Zhang et al., 2018; Kuzukiran et al., 2016) are generally added to remove traces of water in the extract before GC-MS, because water is not compatible with GC columns.

3.3.3. Analysis by chromatographic techniques coupled with mass spectrometry

In the literature (Fig. 6), GC-MS has been used to measure the well-known compounds (PCB, hydrocarbons, OCP, flame retardants), including the most hydrophobic ones. Even if GC-MS has already been used to detect some emerging compounds, LC-MS is the technique usually employed to measure most of the CEC categories. In our database, LC-MS was able to study more compounds than GC-MS (712 vs 593 in Fig. 6), including the most hydrophilic compounds. In Fig. 5, the sum of compounds analysed by GC and LC is greater than 1204 because 126 compounds were measured by two or three separate methods, such as example PAH, organophosphate flame retardants, and UV filters present in PCP or plasticizers.

To analyse with GC-MS, compounds measurable by LC-MS, a fastidious derivatization step is often necessary. To do so, N-tert-butyl-dimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) or N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) can be used for silylation,

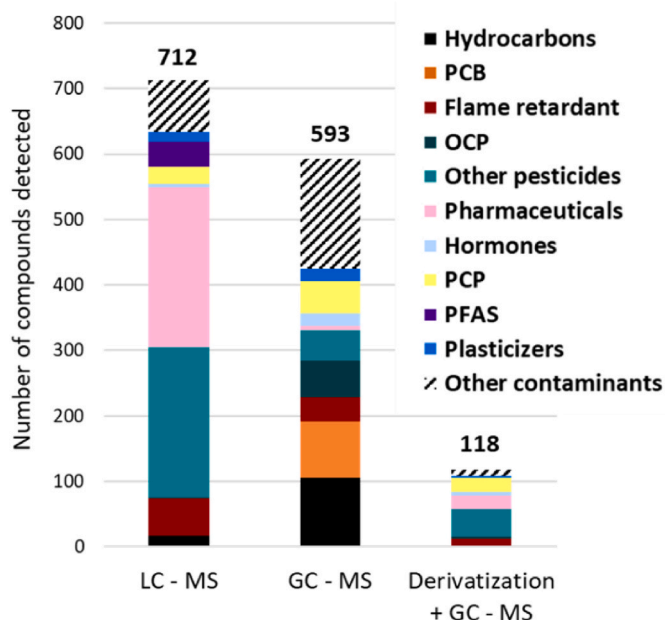


Fig. 6. Number of compounds detected per category as a function of chromatographic method.

making the compounds less polar and more volatile before GC-MS. This was done for the NSAID naproxen and diclofenac (Chakraborty et al., 2019; Gumbi et al., 2019) and the pesticides simazine and diuron (Chiaia-Hernández et al., 2020a). Here, 118 compounds were detected in GC-MS after a derivatization step.

Varying the ionisation methods between chromatography and mass spectrometry enables to detect other compounds not measurable with the usual ionisation techniques. A huge majority of GC-MS studies used electronic impact ionisation (EI). However, polyhalogenated carbazoles, for example, have only been analysed with electron-capture negative ionisation (ECNI). Other compounds, mainly halogenated substances, were analysed by both EI and ECNI-GC-MS, i.e. PCB (Liu et al., 2021), the chlorinated flame retardants mirex and dechlorane 602 and 603 (Zhao et al., 2017a), OCP (García-Solorio et al., 2022) and PBDE (Wan et al., 2020; Liu et al., 2021). With LC-MS, the main way of creating ions is electrospray ionisation (ESI). Nevertheless, Zhu et al. (2013) used atmospheric-pressure chemical ionisation (APCI) to detect halogenated flame retardants, and Peng et al. (2016b) detected brominated and iodine compounds with APCI in negative ionisation coupled to HRMS (Peng et al., 2015).

3.4. Analytical strategies depending on instrument resolution

3.4.1. Target, suspect, and non-target strategies

For analysis of organic contaminants, three different strategies can be applied. Target analysis allows to identify contaminants with the highest level of confidence and quantify them using low-resolution MS and analytical standards. Conversely, NTA requires HRMS such as Orbitrap or QTOF mass spectrometry, which are less suitable for quantification. Those are different from HRMS with magnetic sector mass spectrometer, which is the technology of choice for quantifying dioxins or POP-like PCB (Gao et al., 2015). Suspect analysis aims to draw up lists of contaminants potentially present in the sediment, but each one identified with a confidence level lower than with target analysis (due to the absence of analytical standards), using databases. Databases need to at least provide information on mass-to-charge ratio and ideally also the compound fragmentations to support identification. NTA allows to draw a global picture (or molecular fingerprint) of contamination in a sample, with a wide range of un-named compounds visualised by at least their

mass-to-charge ratio and chromatographic retention time. Out of the 163 papers studied, 144 used only target analysis, 13 used suspect analysis (of which 7 used both target and suspect analysis), and 6 used NTA only.

Based on the papers selected, target analysis detected an average of 17 compounds belonging to just one or very few chemical families. Only a few authors (Škrbić et al., 2018; Babić et al., 2018) targeted a wide range of compounds, i.e. 940 and 428 contaminants respectively, in surface sediments. Babić et al. (2018) and Škrbić et al. (2018) quantified 104 and 313 contaminants in sediments from Sava river in Croatia, close to highly industrial and urbanised areas (Zagreb). Škrbić et al. (2018) revealed 150 contaminants in sediments from 10 different sites submitted to various industrial activities, such as a cardboard production facility, an oil refinery, a solid waste landfill, and meat processing industries, and all influenced by various wastewater effluents.

In this bibliographic research, only 13 studies performed suspect analysis (7 with GC-HRMS and 6 with LC-HRMS) in freshwater sediments. Compounds were identified with levels of confidence based on the Schymanski scale (Schymanski et al., 2014). Level 1 means confirmation with analytical standards, level 2 means a probable structure, and level 3 means an indication of the class of compound but no consensus on the exact structure. In our database, we only consider compounds detected with a level 1 or level 2 confidence. For example, Lübeck et al. (2020) confirmed the presence of 2-mercaptopbenzothiazole in sediment from Copenhagen using analytical standards (level 1), whereas butylated hydroxytoluene was not confirmed but only identified as present based on spectral evidence (level 2).

Suspect analysis can be performed with GC-HRMS to focus on one category of contaminants, as in Kaiser et al. (2012) who detected 5 PCP, or several categories of contaminants, as in Chiaia-Hernández et al. (2020) who detected 69 contaminants spanning 7 categories including both CEC and well-known compounds, such as pharmaceuticals, PCP, hydrocarbons, plasticizers, flame retardants, and other contaminants. Chamorro et al. (2013) detected 33 compounds that had never before been referenced in sediments, such as the pharmaceutical calamenene, the PCP azulone and aromadendrene, and the hydrocarbon retene. Lee et al. (2019) identified 37 compounds (mainly categorized as “other contaminants” in our database) in sediments from Arctic environments, and 26 of these compounds had not been reported in any of the other 162 articles. Identification can be completed with a semi-quantification strategy, using low resolution MS and calibration curves obtained with analytical standards of similar structures in order to evaluate concentrations, as done by Bu et al. (2014) for 70 contaminants in Haihe river in China, using a database of 847 compounds.

Chiaia-Hernández et al. (2013) used suspect analysis with LC-HRMS to explore CEC in sediment cores, and identified quaternary ammonium, methyltriclosan, triclocarban and dichlorocarbonyl before quantifying them with target analysis. HRMS is therefore useful to detect transformation products, in this case methyltriclosan, a transformation product of triclosan. Souchier et al. (2015) used the same strategy to identify the antimicrobial transformation product 1,3-bis(3,4-dichlorophenyl)urea. Suspect analysis can also be focused on a specific category of compounds to detect unusual ones: Nejumal et al. (2018) studied 11 PAH in sediments from Svalbard, a Norwegian archipelago first used as a base for whalers and later for coal mining. Among these 11 PAH, 2-mercaptopbenzothiazole and dibenzothiophene, which are not on the US EPA's list of 16 PAH, were only detected with suspect screening. Lübeck et al. (2020) also detected these two compounds using suspect screening, but with GC-HRMS. They also detected several methylated PAH. Munoz et al. (2016) focused on PFAS in six watersheds in France and used target analysis to quantify common PFAS (PFOA, PFOS, PFNA, etc.) followed by suspect screening to detect PFAS with outstanding structures, such as N,N-dimethyl-3-(perfluorooctanamido)propan-1-amine oxide or N,N,N-trimethyl-3-(perfluorooctylsulfonamido)propan-1-aminium. Ye et al. (2021) used the same strategy on phosphate flame retardants: they used target analysis to cover the classic compounds like tris(2-chloroethyl)

phosphate, and then used suspect analysis to identify 15 other phosphate flame retardants in sediments from Taihu lake in China.

Six authors performed NTA, and all with LC-HRMS analysis. LC-HRMS has the key advantage of using soft ionisation methods (ESI or APCI) that do not destroy the parent ions, unlike GC-HRMS using EI. Peng et al. (2015) used LC-HRMS to focus on natural and synthetic organo-bromine compounds (NSOBC) in surface sediments from lake Michigan: they first they detected 2520 compounds and then potentially identified 1593 NSOBC. Peng et al. (2016b) then also used NTA to study natural and synthetic organo-iodine compounds (NSOIC) and detected more than 3000 compounds in sediments from the Arctic and lake Michigan. Peng et al. (2015, 2016a, 2016b) implemented LC-HRMS with APCI ionisation and looked at the fragments specific to iodine compounds for NSOIC ($m/z = 126.9045$) or bromine compounds for NSOBC ($m/z = 78.9171$). For NSOBC detection, they also used the specific isotopic pattern of the parent ion of chemicals containing bromine.

Statistical processing is needed to interpret all HRMS data. Peng et al. (2016a) performed hierarchical cluster analysis (HCA) to reveal different groups of NSOBC according to their intensity variations in sediment cores. As a result, they were able to highlight two groups of 515 and 768 NSOBC with increasing concentrations since 1950, which testifies that these compounds were likely introduced by human activities, but does not provide firm identification. Chiaia-Hernández et al. (2017) also performed HCA on sediment cores, taking in account all peaks detected by LC-HRMS. They identified four groups of compounds with different temporal trends, and linked these results to the construction and improvement of a WWTP in the upstream area. Chiaia-Hernández et al. (2020b) applied the same HCA-based grouping strategy to assess pesticide contamination in cores from lake Moose in Switzerland. They highlighted the fungicide difenoconazole and the herbicide prosulfocarb belonging to a cluster of 198 compounds that increased in concentrations since the 1990s. Finally, Chiaia-Hernández et al. (2014) worked on core samples from lake Greifensee and lake Lugano and looked in detail at peaks seen with LC-HRMS with both positive and negative ionisations. After removing non-relevant peaks (from noise, in blanks, and without isotopic patterns), about 5% of peaks with positive ionisation and 10% with negative ionisation were retained as suitable for structural elucidation. Within these remaining peaks, they identified the mothproof agent flucufuron and hexachlorophene, a bactericidal agent used in pharmaceuticals and PCP products. It triggered the Morhange talc affaire that causes the death of 36 babies in the 1970s in France.

3.4.2. Data treatment and processing tools

The most popular database for suspect analysis using GC-HRMS is NIST. However, teams can build their own databases. Lee et al. (2019) used a home-made database of 215 compounds with retention times, fragments, and isotopic patterns in parallel to NIST, and identified 37 compounds with the homemade database and 59 with NIST. Ye et al. (2021) obtained spectra from the literature and found 95 organophosphate ester compounds. Minten et al. (2011) also perform suspect screening using an in-house database, but with LC-HRMS to detect 17 substances including pharmaceuticals. ThermoFisher Scientific, Waters Corporation, Agilent Technologies and other big suppliers also propose databases to help screen more contaminants, and there are also public databases like Chemspider or MassBank that contain both LC-HRMS and GC-HRMS spectra. Note that MassBank contains spectra from a lot of device configurations: GC-EI-HRMS, GC-APCI-HRMS, LC-ESI-HRMS, LC-APCI-HRMS, LC-APPI-HRMS, LC-MALDI-HRMS, and more (Horai et al., 2010). Finally, tools like Metfrag or CFM-ID allow to perform *in silico* fragmentation prediction. Chiaia-Hernández et al. (2017) used several databases with fragmentation prediction (MetFrag, PubChem, ChemSpider, MassBank North America) to identify the pesticide imazalil (synonym enilconazole), whose identity was confirmed with analytical standards.

To detect peaks in HRMS data and perform suspect screening, or just

to list peaks corresponding to unknown compounds, operators can use either vendor or open-access software. For suspect screening, vendor softwares are convenient and often chosen. Lee et al. (2019) chose MassHunter (Agilent Technologies, CA), Chamorro et al. (2013) chose ChromaTOF (LECO, MI), and Souchier et al. (2015) chose Xcalibur (Thermo Fisher Scientific, MA). However, for non-target screening, open-access software affords more flexibility. Chiaia-Hernández et al. (2013) used the free software Envimass and Peng et al. (2015, 2016a, 2016b) used an in-house R programme, but a lot more open access tools have recently been developed, such as MZmine (Schmid et al., 2023), MS-Dial (Tsugawa et al., 2020), jHRMStoolbox (Van Herwerden et al., 2024), and Patroon (Helmus et al., 2021), etc.

4. Critical considerations and future research needs

Here we reviewed a set of 163 articles capturing the state of the art in methodologies and knowledge on organic contamination in sediments. We could not viably attempt a fully exhaustive review, but we did focus on thoroughly covering studies on CEC using suspect analysis and NTA. Our database ultimately counted 1204 compounds detected at least once, which we have categorized into 11 groups for discussion. These groups vary in size and contain compounds with heterogeneous physicochemical properties. Furthermore, concentrations of individual compounds are not strictly comparable since they were obtained in different studies that set out with different objectives. For example, studies employ different sampling strategies (nature and number of sites and compounds) to study temporal/spatial trends and in different contamination contexts (urban/rural area, domestic/industrial/agricultural pressure, before and after remedial actions, etc.). Moreover, the analytical strategies used (protocols, instruments) can lead to a wide range of limits of quantification for a given compound. Note too that the nature of the sediment (e.g. grain size and organic matter content) can influence the concentrations of target compounds found. And, although marine sediments were not considered, there is significant variability in the nature of sediments studied (SPM, core, lake sediment, estuary, etc.). It is important to keep these considerations in mind when interpreting Figs. 3 and 4.

Despite these limitations, this review highlights a significant gap in knowledge on many CEC, particularly those that are strongly to moderately hydrophilic. We identified 390 hydrophilic compounds (i.e. with a log Kow <3), some of which, such as cotinine or ofloxacin, were found in concentrations higher than 1000 µg/kg dry sediment. Each of these hydrophilic compounds was generally only reported in one or two studies. Further research therefore needs to explore hydrophilic contamination even in sediment. There are also clearly issues surrounding compounds that have not yet been screened, and other unknown substances (e.g. degradation products, PFAS, pharmaceuticals and PCP, plasticizers, and so on). To our knowledge, this is the first review to address and reference such a large number of contaminants in sediments and to compile all the available data on the methods used and the concentrations and nature of the compounds found (database available in Supplementary material S2). The outputs from this review supports the idea of ubiquitous surface sediment contamination by a wide range of organic micropollutants, in patterns that reflect contemporary trends in consumption. Note too that sediment cores provide an opportunity to investigate temporal trends, as they serve to archive chemicals over time in the form of superimposed layers.

LC-ESI-HRMS emerges as the preferred method for exploring highly to moderately hydrophilic CEC. However, diversifying analysis with less-used ionisation techniques such as APCI for LC-MS or ECNI for GC-MS and performing both LC and GC on the same sample are useful ways to cover an even broadly range variety of compounds potentially present in sediments. For example, GC-EI-MS can capture OCP and PCB, GC-ECNI-MS can capture polyhalogenated carbazoles, and LC-APCI-MS can capture hydrophobic compounds such as phosphorous flame retardants, which makes it essential to further develop spectral databases

with fragments to serve for identifying molecules. Indeed, MassBank contains over 6000 entries for LC-ESI-QTOF but fewer than 100 for GC-APCI-QTOF. Moreover, shared databases referencing newly-detected environmental contaminants would be very useful. Such databases need to contain metadata on identification evidence (e.g. fragments, Rt, mass error) as well as details on the acquisition methods used, especially for suspect screening. A high-resolution spectrometer such as an Orbitrap running in data dependent acquisition mode would be less prone to false-positive identification compared to a QTOF probe running in full scan acquisition mode. The next challenge is then to set criteria to give a level of confidence in identification whatever the methods and instruments used. The Schymanski scale offers a solid framework, but it still leads to different possible interpretations since spectrometer resolution and fragmentation methods are not considered.

Retrospective HRMS analysis of digitally-stored sediment samples is a promising way to screen for newly-discovered compounds in old samples. With full-scan acquisition, all the data is captured and catalogued without the risk of degradation inherent to physical samples. The development of digitally-stored samples using HRMS raises the need of new standardized quality controls commercially available for laboratories (Hollender et al., 2023; Pourchet et al., 2020). For example, Aalizadeh et al. (2021) suggested a mix of common standards to assess an Rt index for detected compounds to enable comparison between different reversed-phase liquid chromatographic methods. The digitally-stored samples using HRMS also raises the issue of big data storage. Data volumes can be reduced by centroidation and conversion of HRMS data to an open file format such as “.mzXML” that is compatible with open-access data processing tools. The emergence of open-access softwares such as MZmine, MS-Dial, jHRMStoolbox, Patroon, etc., enables greater flexibility and accessibility at low cost, as well as comparability and transparency in HRMS data processing. Softwares developments from the HRMS user community are rapidly evolving, bringing additional tools for Rt or fragment prediction to screen contaminants or their transformation products based solely on potential structures (Rocco et al., 2022). In complex environmental matrices such as sediments, a contaminant can easily be missed due to matrix effects. Conversely, natural products may exhibit similarities with contaminants. Software packages produce many false positive identifications that thus require time-consuming manual verifications by experts. Artificial intelligence could play a significant role here in improving the quality checks on fragment peaks, Rt alignment, and other factors. The metabolomics community already uses artificial intelligence solutions for biomarker detection (Ledesma et al., 2021) and is exploring its use as a tool for monitoring drinking water (Samanipour et al., 2019; Vosough et al., 2024). Even though suspect and NTA approaches are valuable for exploring sediment contamination, they do not provide concentration data. Then, further effort is needed to develop semi-quantification for data from suspect analysis (e.g. Munoz et al. (2016) for PFAS). Nevertheless, target analysis remains an essential complement to suspect analysis and NTA approaches to confirm substance identity and provide reliable concentration data.

CRedit authorship contribution statement

Tom Ducrocq: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sylvain Merel:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Data curation, Conceptualization. **Cécile Miège:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization.

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.

Data availability

A database including relevant information retrieved from the set of articles is available in Supplementary material 2 (S2).

Acknowledgments

This review was conducted within the Rhône Sediment Observatory (OSR), a multi-partner research program funded through the Plan Rhône by the European Regional Development Fund (ERDF), Agence de l'eau RMC, CNR, EDF, and three regional councils (Auvergne-Rhône-Alpes, Région Sud – PACA, and Occitanie).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2024.143275>.

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