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Onoja, Simeon; Nel, Holly A.; Abdallah, Mohamed Abou Elwafa; Harrad, Stuart

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1	Microplastics in freshwater sediments: analytical methods, temporal trends, and risk of
2	associated organophosphate esters as exemplar plastics additives
3	
4	Simeon Onoja, Holly A. Nel, Mohamed Abou-Elwafa Abdallah, Stuart Harrad*
5	
6	School of Geography, Earth, and Environmental Sciences,
7	University of Birmingham,
8	Birmingham B15 2TT,
9	UK
10	*Corresponding author: S.J.Harrad@bham.ac.uk

11 Abstract

It has been estimated that over 28 million tonnes of plastics end up in water bodies annually. 12 These plastics degrade into microplastics (MPs), which along with microbeads and MPs from 13 other sources such as wastewater treatment plants continue to threaten the aquatic system. At 14 such small sizes, and corresponding larger surface areas per unit mass/volume, MPs exhibit 15 enhanced capacity for absorbing and desorbing toxic chemicals/additives. Therefore, MPs can 16 serve as vectors through which additives as well as other persistent, bio-accumulative, and 17 toxic chemicals can enter the food chain. Additives are a significant component of most plastic 18 products with some identified as hazardous to health and the environment. One group of 19 additives that has continued to attract interest is organophosphate esters (OPEs), which are 20 used both as flame retardants and plasticizers. Some of these OPEs are suspected carcinogens 21 and endocrine disruptors and have been reported to exert serious toxic effects on freshwater 22 biota. Separate studies on the presence and fate in the freshwater environment of these additives 23 and MPs have emerged recently. However, no studies exist that examine the extent to which 24 plastics additives such as OPEs in sediments are sorbed to MPs as opposed to the sediment 25 itself. This has potentially important implications for the bioavailability of such additives and 26 studies to examine this are recommended. This paper reviews critically the current state-of-27 knowledge on MPs in freshwater sediments, methods for their analysis, as well as their 28 occurrence, temporal trends, and risks to the freshwater aquatic environment. Moreover, to 29 facilitate the study of additives associated with MPs that have been extracted from sediments, 30

31 we consider the possible effect of MP isolation methods on the determination of concentrations32 of associated additives like OPEs.

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Keywords: Microplastics, freshwater sediment, organophosphate esters (OPEs), plasticizers,
flame retardants, analytical methods.

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37 1. Introduction

The littering effect of human activities on water bodies can be traced back to over a hundred 38 and forty years ago (Verne 1998). Today the concern has mounted as the list of harmful 39 substances threatening the hydrosphere (which sustains nearly half of global primary 40 production and serves as habitat to millions of aquatic species) continues to increase 41 (Dümichen et al. 2015; Field et al. 1998; Ibe and Kullenberg 1995). These substances are 42 associated with materials including medical waste, cigarette filters, fishing nets, and plastics 43 which have recently become the focus of increased environmental/health concern. About 19 to 44 23 million metric tonnes (11%) of plastic wastes generated globally in 2016 ended up in aquatic 45 ecosystems (Borrelle et al. 2020) and it is estimated that the global mismanaged plastic waste 46 would be approximately 155 to 266 million metric tonnes by 2026 (Everaert et al. 2018; 47 Lebreton and Andrady 2019). That would mean an estimated 17 to 29 million metric tonnes of 48 these mismanaged plastic wastes ending up in aquatic systems. The Great Lakes alone have 49 been reported to receive around 10,000 tonnes of plastics annually (Hoffman and Hittinger 50 2017), making the problem of plastic pollution in freshwater systems as serious as in marine 51 environments. 52

Plastics enter the aquatic environment from a wide range of sources. Over time, they degrade 53 through photolytic, mechanical, and biological processes into sizes smaller than 5 mm at which 54 point they are referred to as microplastics (MPs) (Arthur et al. 2009). MPs that originate from 55 the degradation of originally larger plastic items are referred to as secondary MPs, while those 56 released directly into the environment in the micro size range (< 5 mm size) are described as 57 primary MPs (Boucher and Friot 2017). Whether primary or secondary, MPs in aquatic 58 environments will either become suspended in the water column or accumulate within 59 sediments (Woodall et al. 2014). Additionally, due to their smaller sizes and corresponding 60 larger surface areas per unit mass/volume, they may exhibit a greater tendency towards 61 adsorbing and desorbing toxic chemicals/additives (Mason et al. 2016). A wide range of 62

additives such as plasticizers, pigments, fillers/extenders, and flame retardants are often
incorporated in plastics during manufacture to give them specific properties. The problem
however is that some of these additives-which make up approximately 50% of some plastic
products (Hartmann et al. 2019; Nel et al. 2021b) have been found to be hazardous to health
and the environment (Lai et al. 2015; Pantelaki and Voutsa 2019).

The risk of MPs transporting plastic additives as well as other persistent, bio-accumulative, 68 and toxic (PBT) chemicals into the food chain upon ingestion by aquatic and terrestrial 69 organisms has become a subject of great concern (Guimarães et al. 2021). Assessment of such 70 risks is complex given the risks are due not only to MPs themselves, but to associated chemical 71 additives. Thus, discerning the impacts of MPs from those of additives present in those MPs, 72 73 as well as those of additives leached from MPs and larger plastic waste into the environment, is an important research goal. Organophosphate esters (OPEs), which are used both as flame 74 retardants and as plasticizers are one of the most important and widely-used plastic additives 75 (Herrera et al. 2003; Wang 2000). Chlorinated OPEs such as tris(2-chloroethyl) phosphate 76 (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), and tris(1,3-dichloro-2-propyl) phosphate 77 (TDCIPP) are mostly used as flame retardants, while the non-chlorinated alkyl-, aryl-78 phosphates are often used as industrial lubricants and as plasticizers (Zeng et al. 2018). OPEs 79 have been associated with serious health and environmental concerns (Table 1). Beyond 80 environmental persistence, the possibility of some- OPEs (mostly the chlorinated alkyl 81 phosphates) (Kawagoshi et al. 2002; Shi et al. 2018) being carcinogenic as well as posing a 82 risk of other such serious health concerns as infertility and neurotoxicity have been reported 83 (Hoffman et al. 2017; Hou et al. 2016; Van der Veen and de Boer 2012, Stapleton et al. 2009; 84 WHO 1993). Decreased semen quality and other fertility problems have been associated with 85 TDCIPP and triphenyl phosphate (TPHP) (Stapleton et al., 2009) while tris(methyl-phenyl) 86 phosphate (TMPP) and triphenyl phosphate (TPHP) have both displayed neurotoxic potential 87 in zebra fish larvae (Shi et al., 2018). TCEP has been classified as a category 2 reproductive 88 toxicant and category 2 carcinogen (EU 2009). Another area of concern is the effect of the 89 alcohols released as a result of hydrolysis of some of these OPEs, as it has been confirmed that 90 butoxyethanol produced by the hydrolysis of tributoxy ethyl phosphate (TBEP), is not just a 91 mutagen but also an endocrine disruptor (Boatman et al. 2004). Overall, the ecotoxic effects of 92 several chemical plastic additives including flame retardants and plasticizers are well-93 94 documented in the literature. Therefore, the enhanced release of these hazardous chemical additives to the aquatic environment from MPs due to their large surface area to mass/volume 95

96 ratios and subsequent toxic impacts on aquatic organisms is highly concerning. Most recent 97 reviews have focused on sources/abundance, environmental impact, fate, and transport of MPs 98 (Choong et al. 2020; Chowdhury et al. 2020; Koutnik et al. 2021), however, not many have 99 looked at plastic additives and to the best of our knowledge, none have considered the possible 100 impact of MP isolation methods on measurements of plastic additives like OPEs.

101 It is against this backdrop that this paper provides a critical review of the current state-of-102 knowledge on MPs in freshwater sediment including MPs occurrence, temporal trends, and 103 potential risk to the aquatic environment. Methods for the analysis of MPs in freshwater 104 sediment are reviewed, including consideration of the impact of such methods on 105 measurements of additives like OPEs in MPs isolated from sediments. Finally, research gaps 106 are highlighted and recommendations for future research are presented.

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Table 1: Names, abbreviations, Structures, CAS Numbers, molecular formula, application environmental/health hazard of some OPEs (SigmaAldrich, 2021, Wei et al., 2015, Van der Veen and de Boer, 2012, Reemtsma et al., 2008, Hawley and Lewis Sr, 2001, Cadogan and Howick,
2000).

COMPOUND	ABBR.	STRUCTURE	CAS NO.	MOLECULAR FORMULA	APPLICATIONS	ENVIRONMENTAL/HEALTH HAZARD
Tris (chloroethyl) phosphate	TCEP		115-96-8	$C_6H_{12}Cl_3O_4P$	Flame Retardant, Plasticizer, Lacquer Paint, Glue, Industrial processes	Carcinogenic, highly toxic, environmentally persistent, and cytotoxic in high concentration
Tris (2- chloroisopropyl) phosphate	TCIPP		13674-84-5	C9H18Cl3O4P	Flame Retardant, Plasticizer	Suspected carcinogen, and cytotoxic in high concentration
Tris (1,3-dichloro-2- propyl) phosphate	TDCIPP		13674-87-8	C9H15Cl6O4P	Flame Retardant, Plasticizer, Lacquer Paint, Glue	Carcinogenic, Developmental, and reproductive toxicity, endocrine disruption
Tris(2-chloro-ethyl) phosphite	CLP1	Cl Cl O P O Cl	140-08-9	$C_6H_{12}Cl_3O_3P$	Flame Retardant, Stabilizer and Hydraulic fluids, and Industrial processes	Suspected carcinogen, Reproductive toxicity
Trimethyl phosphate	TMP	H ₃ C H ₃ C H ₃ C CH ₃	512-56-1	C ₃ H ₉ O ₄ P	Industrial processes	Genotoxic, possible reproductive toxicity

Triethyl phosphate	TEP	О H ₃ C_O-Р-O ^C CH ₃	78-40-0	$C_6H_{15}O_4P$	Plasticizer, Catalyst, ethylating agent, Raw material for insecticides	Possible developmental and reproductive toxicity
Tripropyl phosphate	TPP	H ₃ C 0 0 CH ₃	513-08-06	C9H21O4P	Flame Retardant, Plasticizer, Hydraulic fluids, Lacquer paint, glue, Cosmetic products and industrial processes	
Tris (isobutyl) phosphate	TIBP	$H_{3}C \xrightarrow{C} CH_{3}$	126-71-6	C12H27O4P	Plasticizers, Hydraulic fluid, Floor finish, wax, lacquer paint, glue, Ant- foam agent and industrial processes	
Tri-n-butyl phosphate	TNBP	0 ^{-/-} СН ₃ H ₃ C ^{-/-} 0 ^{-/} СН ₃	126-73-8	C12H27O4P	Flame retardants, Hydraulic fluid, Plasticizer,	Neurotoxic, suspected carcinogen
Tris (2-butoxyethyl) phosphate	TBOEP	Hic 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	78-51-3	C18H39O7P	Flame Retardant, Plasticizer, floor finish, wax, lacquer paint, glue, anti-foam agent	Suspected carcinogen, developmental toxicity
Tris (2-ethylhexyl) phosphate	TEHP		78-42-2	C24H51O4P	Flame Retardant, Plasticizer and fungus resistant	Not considered to be carcinogenic in humans. Reproductive and developmental toxicity needs to be investigated.
2-Ethylhexyl diphenyl phosphate	EHDPP	С 0-Р С С Н ₃	1241-94-7	C20H27O4P	Flame retardants, Plasticizer, certain food packaging applications	

Tris (phenyl) phosphate	TPHP	115-86-6	C18H15O4P	Flame retardants and Plasticizers	Reproductive and developmental toxicity, Neurotoxicity, genotoxicity, endocrine effect. Bioaccumulation and very toxic to aquatic life
Tris (methylphenyl) phosphate (or Tricresyl phosphate)	TMPP	1330-78-5	$C_{21}H_{21}O_4P$	Plasticizer, flame- retardant, Industrial processes, non- flammable fluid in hydraulic systems and as stabilizers	Neurotoxic, acute toxicity, Hazardous to the aquatic environment,

124 1.1. Risk of MPs and associated additives to the freshwater environment

Despite the focus on the marine environment, MPs have been reported in freshwater systems such as lakes and rivers (Eriksen et al. 2013, Hoellein et al. 2014; Zbyszewski et al. 2014) and the likelihood that the abundance of these MPs in such compartments will continue to increase has been reported by several researchers (Eriksen et al. 2013; Geyer et al. 2017). This increasing trend in MP pollution is accompanied by several risks to the freshwater environment associated with both the MPs and their chemical additives.

131 1.2 Risks associated with MPs.

The environmental persistence of MPs is a subject of great concern as fears exist that they can 132 reside in the environment for hundreds of years once released (Zbyszewski and Corcoran 133 2011), and moreover because of the potential toxic effects of these MPs on biota. The 134 135 neurotoxic potential of MPs has been reported following a study involving zebrafish juveniles (Guimarães et al. 2021). MPs have also been reported to impact adversely on plants as 136 137 decreased root cell viability and growth was observed in a freshwater floating plant (duckweed Lemna minor) following exposure to microbeads (Kalčíková et al. 2017). Adsorption of MP 138 particles to the roots of a vascular plant (Spirodela polyrhiza) has also been reported (Dovidat 139 et al. 2020). Coupled with the fact that these plants form an essential part of the ecosystem, this 140 raises concern over rising MPs concentrations in the freshwater environment. 141

Ingestion of MPs by aquatic organisms has also been reported covering 39 freshwater species 142 (4 fish species and 35 invertebrates) (Scherer et al. 2018). A separate study by Hurley et al 143 144 (2017) showed that sediments play a major role in driving this intake of MPs as *Tubifex* worms ingested a mean concentration of 129 ± 65.4 MP particles/g tissue following their exposure to 145 sediments with concentrations ranging from 56 to 2543 MP particles/kg (Hurley et al. 2017). 146 147 Although egestion has been reported as rapid and effective, MPs tend to remain in guts of fishes and sometimes translocate to internal organs (Parker et al. 2021). The presence of MPs in the 148 guts, stomach, and liver of freshwater organisms such as snails, crustaceans, worms (Imhof et 149 al. 2013), zooplankton (Cole et al. 2013), and fish (Sanchez et al. 2014, McGoran et al. 2017, 150 Silva-Cavalcanti et al. 2017) have also been reported. These ingested MPs not only serve as 151 vectors by which organic and inorganic pollutants are transported into living organisms, (Bakir 152 153 et al. 2012; Koelmans et al. 2013) but they can clog the digestive tract of organisms such as in the Norway lobster Nephrops norvegicus (Murray and Cowie 2011) and zebra mussel 154 Dreissena polymorpha (Magni et al. 2018) and eventually lead to death (Barnes et al. 2009). 155

Reduced feeding in zooplankton (Cole et al. 2013) and lugworms (Besseling et al. 2013) as well as decreased fecundity for copepods (e.g. *Tigriopus japonicus*) (Lee et al. 2013) has been reported following ingestion of MPs. There have also been reports of plastics in dried fish tissues from four commonly consumed dried fish species (Karami et al. 2017). These and other similar studies show that although the effect of MPs on human health is still unclear, dietary exposure to MPs may be substantial.

162 1.3 Risks from chemical plastic additives associated with MPs.

Some toxic effects of MPs have been attributed to associated additives and sorbed pollutants, 163 with previous studies highlighting the enhanced toxicity of pollutants when they coexist with 164 MPs (Deng et al. 2018; Ogata et al. 2009; Teuten et al. 2009). Rochman et al, (2013) observed 165 less signs of stress in fish fed virgin polyethylene fragments than those fed marine polyethylene 166 fragments (Rochman et al. 2013b); while a separate study has reported embryotoxicity in 167 purple sea urchin (Paracentrotus lividus) following exposure to MP additives leached from 168 micronized plastic toys (Oliviero et al. 2019). Furthermore, increased bioaccumulation of 169 polychlorinated biphenyls (PCBs) in zooplankton because of MP ingestion and the possibility 170 171 of biomagnification as these MPs and associated additives move up the food chain has been reported (Mattsson et al. 2017; Teuten et al. 2009). Rochman et al. (2013) also reported 172 173 bioaccumulation of chemical pollutants (polycyclic aromatic hydrocarbons (PAHs), PCBs and polybrominated diphenyl ethers (PBDEs) following ingestion of polyethylene MPs by exposed 174 175 fish species that also suffered liver toxicity due to such exposure (Rochman et al. 2013b). A recent study by Garcia-Garin et al. (2020), detected OPEs in muscle samples of the edible 176 Bogue - Boops boops (Garcia-Garin et al. 2020). Although this study did not correlate the 177 detection of OPEs to MP ingestion, previous studies have recommended Boops boops for 178 179 studies on MP pollution because of the frequent detection of particles in their guts (Bray et al. 180 2019). It is however interesting to note that despite the potential adverse biological effects of OPEs outlined in section 1, there remain to date no studies that have examined the risks to 181 freshwater biota from OPEs associated with sediment MPs. Research to examine such risks 182 from OPEs and other additives is urgently required. 183

184 2. Occurrence of MPs in freshwater sediment

185 In order to investigate research trends in publications studying the occurrence/concentrations 186 of MPs in freshwater sediments between 2000 and 2020, a search was conducted in the *ISI web* 187 *of knowledge* database using different combinations of the keywords "*microplastic*", *"freshwater" and "sediment*". A total of 245 relevant publications were found of which 20%
(49) have been published between 1st of January and 28th June 2021. 31% (77) were published
in 2020, 24% (58) were published in 2019, 13% (33) in 2018 and only 11% (28) between 2017
and 2013 (Figure 1). This illustrates increasing interest in the study of MPs in freshwater
ecosystems.

A notable geographical trend is that over 78% of these studies were conducted in only 7 countries (Figure 2). This shows a serious lack of data on freshwater microplastics for most parts of the world. Only 12 studies were undertaken in Africa (5 in south Africa) even though Africa's 205,670 km² lake area accounts for 14.1% of the world's lake area (Herdendorf, 1982).

197 Between 2015 and June 202, there have been significant improvements in the understanding and measurement of MPs in freshwater sediment (Table 2). The use of microscopy for the 198 identification of MPs was recommended by researchers in 2015 (Masura et al. 2015; Song et 199 al. 2015) and has subsequently become the most common method used. Vaughan et al., (2017) 200 used microscopy to determine the abundance and distribution of MPs in what was described as 201 "the first assessment of microplastics concentration in the sediments of either a small or an 202 urban lake and the first for any lake in the UK". The study reported relatively low 203 concentrations (25-30 particles per 100 g d/w) of MPs in Edgbaston Pool, Birmingham, UK 204 but acknowledged the fact that more recent methods of identification and characterization (e.g. 205 Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy) were not available 206 (Vaughan et al. 2017). Compared to other studies of freshwater lakes across the globe (i.e. 207 Fischer et al. 2016; Su et al. 2016), Yuan et al. (2019a) described Poyang Lake in China as 208 having higher levels (54-506 items/kg dw) and biological risks of MPs. Research has also 209 shown that a combination of one or more methods can enhance the quality of results, as one 210 method can compensate for the disadvantages of another (Hidalgo-Ruz et al. 2012). It is clear 211 from the foregoing that 2017 to 2018 marked an upturn of interest in the study of MPs in 212 freshwater sediments. Therefore, an overview of studies between January 2016 and December 213 2020 provides a more recent and focused perspective of the current trends in the study of MPs 214 in freshwater sediments (Table 2). Furthermore, our focus on recent publications provides 215 216 insights into the current challenge arising from the lack of harmonization in reporting formats and sampling designs that has been identified as a major impediment to elucidating temporal 217 trends in environmental pollution with MPs (Browne et al. 2015; Hanvey et al. 2017; Mai et 218 al. 2018). 219



Figure 1: Number of publications per year on MPs in freshwater sediments between January 2000 and June 2021 (data obtained from ISI
web of knowledge)





226 (Data obtained from ISI web of knowledge)

Country/region	Size range	Concentration of MPs	Trend identified	Gaps identified	Reference
Europe (Germany)	20–5000 μm	Median concentration of 7.57×10^5 p m ⁻³	High MP pollution comparable to the high levels reported in some Asian countries.	Difficulty of data comparisons because of the diversity of analysis and methods used in monitoring studies	Scherer et al. 2020
Europe (Hungary)	≥100 μm	Range from 0.46 to 1.62 particles/kg, and a mean value of 0.81 ± 0.37 particles/kg.	Higher concentrations of the identified polymer types were seen at pond inlet compared to outlet and the concentration of sediment MP in this study were much lower than other international results	Intensive investigation of sediment and water samples is required, and such studies should ensure that all suspected particles are exactly identified using suitable methods such as FTIR as this is missing in most current studies.	(Bordós et al. 2019)
Europe (United Kingdom- London)	1 μm to 500 μm	Approximately 539 particles per kilogram of dried sediment	Relatively low number of MPs were found in older sediments.	Improvements in contaminant reduction measures are highly recommended for future stratigraphic work. Use of more effective microplastic detection methods along with future paleolimnological work to allow a more diverse quantification of historical flux of microplastic wastes in terrestrial, freshwater, and marine environments.	Turner et al. 2019

Table 2: Overview of studies of microplastics in freshwater environments between 2016 and 2020.

Asia (China)	0.03-0.1 mm	821 ± 100 MP/kg to 1936 ± 121 MP/kg	Compared to an earlier study on the same study location (Yuan et al., 2019), A higher concentration of MPs (approximately 4–30 times higher) was reported.	further long-term and systematic studies of the environmental fate of smaller size MPs (<0.1 mm) in freshwater systems.	Jian et al. 2020
Asia (Urban surface waters of Wuhan, China)	50 – 5000 μm.	1660 ± 639 to 8925 ± 1591 number of particles per cubic meter of water (n/m ³)	High heterogeneity was discovered in the concentration of MPs across the study areas.	Comprehensive monitoring of the abundance of microplastics in inland freshwaters is recommended.	Wang et al. 2017
			A decrease in the concentration of MPs with increasing distance from the urban center was discovered.	Further research on accurate determination of MP sources and pollution control strategies is needed.	
			The plastic levels recorded for the rivers were less than for the lakes, likely because of enhanced loss of MPs from rivers as a result of stronger hydrodynamics.	A need for studies of the effect of color on the rate of ingestion of MPs is highlighted	
			Fibrous (52.9 – 95.6%), colored (50.4 – 86.9%) and small (MPs less than 2 mm accounting for more		

			than 80%) MPs were the most dominant.		
Asia (Lake Ulansuhai in China)	Six size categories: < 0.5 mm, 0.5 – 1 mm, 1–2 mm, 2–3 mm, 3– 4 mm and 4– 5 mm	1760 ± 710 to $10,120 \pm$ 4090 number of particles per cubic meter of water (n/m ³)	Spatial distribution of MPs was such that higher levels of MP were recorded at the entrance of a farmland drainage canal with a downward trend towards the end of the drainage canal of the lake	Further studies of the toxic hazard MPs pose to plants and aquatic animals is recommended	Wang et al. 2019
Asia (Poyang Lake China)	<0.5 mm	54 – 506 number of particles per kilogram dry weight (dw)		More accurate and effective studies should be carried out on the impacts and fate of microplastics in freshwater ecosystems. Also, the potential impacts of MP consumption by human beings should be studied	Yuan et al. 2019
Asia (Changsha, China Surface sediments)	<1mm	Ranged from 270.17 \pm 48.23 items/kg to 866.59 \pm 37.96 items/kg (dw)		More research on understanding the environmental behavior of microplastics in urban waters	Wen et al. 2018

Asia (West	macroplastics	From 617 to 2217		Further work is encouraged on the effect of	Jiang et al. 2018
Dongting Lake	(>25 mm) and	items/m ³ and 717 to		hydrodynamic conditions on the distribution	
and South	mesoplastics	2317 items/m ³ in		of microplastics	
Dongting Lake,	(5–25 mm)	surface water of West			
both in China)		Dongting Lake and			
		South Dongting Lake,			
		respectively while the			
		lakeshore sediment for			
		both study locations			
		ranged from 320 to 480			
		items/m ³ and 200–1150			
		items/m ³ , respectively.			
North America (Lake Ontario Canada)	< 2 mm	Approximately 760 particles per Kg dry sediment.	It is likely that fibers are transported through suspension for greater distances than fragments. Some of the previously identified methodological problems in microplastic research have been resolved. However, standardization	Thorough analysis of microplastic morphology and composition may be used to shed more light on the role played by the type of microplastic on the depth to which they are transported in an aquatic environment. Future studies aimed at understanding how microplastic abundance in sediment vary with distance from outfall are	Ballent et al. 2016
			of operational protocol will still require more research.	recommended. This should be done using studies directly adjacent to storm waters,	

				wastewater treatment plants and sewer outfalls. Future monitoring of microplastic in the sediments of Lake Ontario is also recommended	
North America (Lake Michigan, USA)	<1 mm	An average plastic abundance of ~17,000 particles/km ² lake surface area	The relative abundance of fragments shows that secondary sources of microplastics are more significant to this study area than primary sources. The order of abundance of plastic types (polyethylene- mostly high- density being the most abundant followed by polypropylene) is consistent with global trends in the mass production of plastics.		Mason et al. 2016
North America (St. Lawrence River-Canada)	Mostly <400 μm	Concentration of MPs range from 65 to 7562 plastics per kg d/w (mean concentration is 832 (±150 SE) plastics per kg d/w.	Factors such as sediment characteristics, environmental filters and point sources are related to the variation in the distribution, abundance and diversity of microplastics across a large river.	There is the need for a standardized protocol in MP analysis and future studies should look at the mass balance of microplastic loads as well as their fate during transport to the ocean as this will provide answers on whether river sediments are permanent or transient sinks for microplastic pollution	Crew et al. 2020

Africa (Johannesburg South Africa)	53 to 4000 μm	MP abundances range from 4 particles kg ⁻¹ dw to 1347.5 particles kg ⁻¹ dw and mean of 166.8 particles kg ⁻¹ dry weight	Distribution of MPs is influenced by such factors as water depth, flow and obstructions in rivers such as large weirs.	Increased focus on understanding microplastic pollution in South Africa and further studies aimed at understanding the behavior of microplastics in the environment.	Dahms et al. 2020
Africa (Lake Victoria in Uganda)	300-5000 μm	The abundance of MPs ranged from 0 – 108 particles/kg (dw)	Landing beaches were identified as major plastic pollution hotspots as MP concentration for landing beaches far exceed results for recreational areas.		Egessa et al. 2020
Africa (Nigeria)	20 – 5000 μm	MP abundances range from 347 to 4031 items·kg-1 (In dry season) and 507–7593 items·kg $^{-1}$ (In rainy season)	The most common plastic materials found were Polyethylene terephthalate (PET) and Plasticised polyvinyl chloride (PVC P). The least abundant were Polyamide (PA) and Polystyrene (PS).		Oni et al. 2020
Japan Thailand Malaysia South Africa	315 μm–5 mm (Although most were between 315 μm – 1 mm)	Japan: 1900 pieces/kg dry sediment Thailand: 100 pieces/kg dry sediment	For all study locations, there has been an increasing trend in the abundance of MPs from the 1950s to the 2000s.	A more detailed analysis of microplastic pollution with time using more of the core is recommended. To enable a better understanding of the controlling factors behind the difference in	Matsuguma et al. 2017

	Sediment is an important sink for	polymer composition between the different	
	MPs as more MPs were found in	study areas, Analysis of more samples is	
	sediments than the surface water of	recommended.	
	Tokyo Bay.		
	There is a consistency between the		
	trend of microplastic abundance		
	in sediments and the global trend of		
	plastic production.		

229 3. Analysis of MPs in sediment

- The analysis of MPs in sediments requires strict adherence to standard procedures. This is particularly important considering the possibility of post-sampling contaminations (Woodall et al. 2015). Based on published methodology, such impacts were addressed according to the following sub-headings: (1) sampling, (2) extraction, (3) identification / quantification, and (4)
- 234 quality assurance/quality control (Figure 3).



Figure 3: Flow chart of the procedures followed for analysis of MPs in sediments (Pyro-GC/MS: Pyrolysis Gas Chromatography/Mass Spectrometry, TGA-TD-GC-MS:
Thermogravimetric analysis-thermal desorption-gas chromatography-mass spectroscopy,
FTIR: Fourier transform infrared, SEM: scanning electron microscope, RS: Raman
spectroscopy)

241 3.1 Sampling

Several tools and approaches have been employed to sample sediment most of which are 242 dictated by the objectives of the research and the peculiarities of the study location. However, 243 previous reviews on the methods of measuring MPs in sediments (Hanvey et al. 2017; Mai et 244 al. 2018) identified a lack of standardized procedures in sediment sampling, leading to the 245 reporting of data in a variety of units. These units include MP pieces per m² (do Sul and Costa 246 2014; Wessel et al. 2016), pieces per mL or L (Browne et al. 2011; Woodall et al. 2015), or per 247 weight (g or kg) of sediment (Alomar et al. 2016; Klein et al. 2018; Ng and Obbard 2006). This 248 has made it difficult to compare the results of different studies quantifying MP contamination 249 across the world and is further complicated by the density estimation required for conversion 250 251 between such units that can lead to errors (Van Cauwenberghe et al. 2015).

In order to get a more focused view of this subject as it relates to the most recent studies, the 252 keywords "Sediment sampling for microplastics in freshwater" were used to search the entire 253 database of the ISI Web of Science for relevant studies between 2018 and 2020. The result was 254 then narrowed down to seventeen (17) publications from different regions of the world using 255 such criteria as year of publication and relevance to the topic of interest. For sampling below 256 surface sediment, eight of the studies used Van Veen or other grab samplers (Baldwin et al. 257 2020; Crew et al. 2020; Eo et al. 2019; Ramírez-Álvarez et al. 2020; Rodrigues et al. 2018; 258 259 Scherer et al. 2020; Shruti et al. 2019; Xu et al. 2020) and one used a box corer (Pagter et al. 2020). For surface sediment sampling, metal hand scoop (Schessl et al. 2019), stainless-steel 260 shovel (Jiang et al. 2018; Peng et al. 2018), metal pail shovel (Deng et al. 2020; Ramírez-261 Álvarez et al. 2020), stainless steel split spoon or Ekman dredge (Eo et al. 2019; Wilkens et al. 262 2020), garden spade (Mani et al. 2019; Peller et al. 2019) and stainless-steel spatula (Toumi et 263 al. 2019) were used. This further confirms the lack of standardization between sampling 264 methods while showing that the box corer seems the most common approach to depth 265 sampling. It is clear though, that the choice of equipment and sampling procedure is often 266 governed largely by the nature of sediments to be sampled and the accessibility of the sampling 267 site. A further consideration is that secondary contamination by MPs can be avoided by use of 268 269 non-plastic sampling tools (Jiang et al. 2018; Wen et al. 2018).

270 **3.2.** Extraction

Once sediment samples are collected and transported to a laboratory for analysis, the next objective is to separate the MPs from a complex matrix of other organic and inorganic materials. A standard method for doing this is yet to be established (Horton et al. 2017) but most recent studies seem to employ a combination of size and density separation techniques (Vaughan et al. 2017). The use of fluidization/elutriation (another density-based technique) has also been reported in some recent publications (Claessens et al. 2011; Kedzierski et al. 2016; Nuelle et al. 2014; Zhu 2015).

278 Most of the reviewed studies employed varying mesh sizes including: 8 μ m to 47 mm (Zhang 279 et al. 2019), and 90 μ m to 4.75 mm (Pan et al. 2019); it is however recommended that the 280 choice of mesh size should be such that it allows the collection of a wide size fraction, while 281 minimizing clogging of mesh holes (Mai et al. 2018).

The second approach is density separation, this approach takes advantage of the low density of 282 most plastic materials $(0.9 - 1.55 \text{ g/cm}^3)$. In a review of 48 studies from 18 different countries, 283 284 Hanvey et al. (2017) reported the application of density separation in 84% of studies. This is partly because recovery rates as high as 100% have been previously reported (Mai et al. 2018). 285 The basic idea behind this approach is allowing the MPs to float in a high-density solution 286 thereby permitting the MPs to be filtered out. Four main steps have been identified, 287 specifically: (1) introduction of an aqueous solution of known density, (2) manual or 288 mechanical shaking/stirring for a specific period, (3) allowing time for settling and 289 equilibration, and (4) filtration (Hanvey et al. 2017). The aim of shaking or stirring after 290 introducing the solution is to ensure that the MPs are properly separated from other sediment 291 particles. This can either be done manually, (Wang et al. 2019; Zhang et al. 2019), or 292 293 mechanically using a vortex mixer (Woodall et al., 2014) or mechanical shaker (Ng and Obbard, 2006). The time allowed for equilibration and settling after the shaking can be as short 294 295 as five minutes (Corcoran et al. 2015), or up to 12 hours (overnight) (Stolte et al. 2015). There are a variety of high-density solutions that can be used for the first step and a recovery rate of 296 80-100% has been reported for NaCl solution (Fries et al. 2013), 96-100% for ZnCl₂ solution 297 (Imhof et al. 2012) and 94 – 98% for NaI solution (Claessens et al., 2013). Turner et al., 2019 298 299 used sodium polytungstate (SPT) solution to achieve a density as high as 2.2 g/cm³, suitable for the extraction of high-density plastics such as polytetrafluoroethylene $(2.08 - 2.17 \text{ g/cm}^3)$ 300 and polyvinylidene fluoride or polyvinylidene difluoride (1.79 g/cm³) (Turner et al., 2019a). 301

The use of water for density separation reported a low recovery rate of less than 70% (Quinnet al. 2017).

As an alternative to the density-based techniques, an oil extraction protocol has been reported (Crichton et al. 2017). This cost-effective alternative had a reported recovery rate of 92.7% \pm 4.3% for fibers and 99% \pm 1.4% for particles. In recent times, the use of techniques capable of providing recovery rates as high as 100% has also been reported. These include the use of pressurized fluid extraction (which has provided recovery rates between 101 and 111%) (Fuller and Gautam 2016) and air-induced overflow (91 – 99%) (Nuelle et al. 2014)

Following the removal of all or most of the inorganic materials such as silicates, the next step is the filtration or wet sieving of the mixture. This is meant to separate suspended low density MPs from other components of the solution. This separation is principally achieved by sieving or vacuum filtration and for most studies, the use of stainless-steel sieves or glass fiber filters is the norm (Mai et al., 2018). Just as for dry sieving, the choice of mesh size should be such as allows the collection of a wide range of size fractions and minimizes clogging of mesh holes.

316 Digestion of organic matter may improve MP detection accuracy and remove interference during polymer identification (Prata et al. 2019) with several methods used by previous 317 researchers (Table 2). In a review of over 60 publications, Prata et al (2019) reported that 60% 318 did not carry out any form of purification, 35% used H₂O₂ and 15% used Fenton's reagent (a 319 solution of H₂O₂ with ferrous iron as a catalyst). Two other reviews Mai et al. (2018) and 320 Hanvey et al. (2017b) concluded a solution of 30% H₂O₂ to be the method of choice for this 321 process. This is because it is very effective in dissolving higher molecular weight organic 322 matter, while leaving the physical properties of the MPs intact (although it has been speculated 323 that changes in the color of MPs are possible) (Mai et al., 2018). 324

Method	Description	Disadvantage	Reference
Acid digestion	Use of acids such as nitric acid (55% HNO ₃) and hydrochloric acid (37% HCl) to degrade organic matter	Risk of digesting some low resistance MPs such as nylon and polyethylene terephthalate at high acid concentration and temperature	(Qiu et al. 2016)

325	Table 3: Methods	for separating	sediment MPs from	n organic and	inorganic matter
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Alkali digestion	Use of alkali such as potassium hydroxide (10% KOH) and sodium hydroxide (20 -50% NaOH) for the digestion process	Risk of damage or discoloration of MPs	(Mai et al., 2018), (Qiu et al. 2016)
Oxidizing agents	Use of oxidizing agents such as hydrogen peroxide (35% H ₂ O ₂). Sometimes combined with NaOH and HCl for better performance.	Shrinkage of certain plastics has been observed.	(Prata et al., 2019)
Enzymatic digestion	This involves the use of enzymes such as proteinase K (500 mg/mL) for organic matter digestion.	No known risk to the integrity of MPs associated with this method yet, but its application is not as straightforward as chemical digestion methods	(Karlsson et al. 2017)
Other Methods	Use of microwaves and ultrasonication	High risk of damage to the MPs.	(Karlsson et al., 2017), (Yiying et al. 2009)

326

327 3.3. Identification/quantification

The identification and quantification of MPs often begins with their isolation from non-plastic 328 329 particles based on physical properties that are unique to plastics. The process of identification based on physical properties such as morphology and color are called visual inspection or 330 331 visual sorting. This approach - conducted using a microscope - has proven rather ineffective, as reports exist of over or underestimation (Nel et al. 2021a; Cheung et al. 2016; Lenz et al. 332 2015; Löder et al. 2015). For example, in one reported instance, 32% of particles and 25% of 333 fibers were wrongly identified using visual inspection (Lenz et al., 2015). Another study, 334 reported that 20% of particles identified as MPs by visual sorting, were later identified as 335 aluminum silicate after viewing with a scanning electronic microscope (Eriksen et al. 2013). 336 Other more effective approaches have been reported. These include: Raman spectroscopy 337

338 (Käppler et al. 2016), FTIR (Peng et al. 2017), scanning electron microscopy (Eriksen et al.
339 2013), pyrolysis-gas chromatography-mass spectrometry (PyroGC-MS) (Fischer and Scholz340 Böttcher, 2017) and thermal desorption gas chromatography-mass spectrometry (TD-GC/MS)
341 (Altmann et al. 2019).

342 3.3.1 Raman Spectroscopy

Raman spectroscopy is non-destructive and can be used for both identification and quantification of MPs (Hanvey et al. 2017). It has been used successfully to identify and quantify MPs down to as small as 1 μ m (Pan et al., 2019, Lenz et al., 2015). Other advantages of this method include the ability to generate information on the chemical composition of the MPs and other associated organic and inorganic matter (Klein et al. 2018).

348 3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

According to Hanvey et al. (2017b), 23 out of 43 studies reviewed used FTIR. The use of FTIR 349 has also been reported in other forms such as micro-FTIR (Vianello et al. 2013) which is 350 basically a combination of optical microscopy and FTIR and attenuated total reflectance (ATR) 351 352 FTIR (Cheung et al. 2016). The advantages of this method include its high throughput efficiency and non-destructive nature. It is however limited to measuring particles of sizes 353 around 25 μ m and thickness < 100 μ m. There is also the possibility of an overlap of polymer 354 bands which make it difficult to distinguish between identified polymers (Käppler et al. 2016; 355 356 Käppler et al. 2018).

357 3.3.3 Scanning Electron Microscopy (SEM)

The use of scanning electron microscopy for identification of MPs has gained popularity for several reasons such as its ability to provide clear images of vital physical properties of the afo particle (Hanvey et al. 2017). It is good for showing physical degradation such as pits and cracks and mong other advantages and has been reported to be useful in differentiating between MPs and other organic/inorganic components (Crawford and Quinn 2017). It has also been combined with energy-dispersive X-ray spectroscopy (SEM-EDS) to examine the composition as well as additive content of plastics (Crawford and Quinn 2017; Fries et al. 2013). The laborious preparatory processes involved in using this method is however a major disadvantage (Wang et al., ace 2017).

367 3.3.4 Pyrolysis-gas chromatography - mass spectrometry (PyroGC-MS)

The basic principle of this method involves thermal decomposition of the particle of interest, followed by identification of the cryo-trapped evolved gases using mass spectrometry (Dümichen et al. 2017; Shim et al. 2017). This method is not only useful in identifying MPs but very effective for determining the polymer type, as well as associated organic matter (Mai et al. 2018). However, it is time consuming and destructive (Mai et al., 2018), and has difficulty correctly identifying polymers with polar sub-units (Dekiff et al. 2014a; Fries et al. 2013; Käppler et al. 2018).

375 **3.3.5** Thermogravimetric Analysis coupled with Thermal desorption gas 376 chromatography with mass spectrometric detection (TGA-TD-GC/MS)

TGA-TD-GC/MS works basically by interfacing thermo-gravimetric analysis connected to a
solid-phase sorbent, with thermal desorption GC/MS (Dümichen et al. 2017; Elert et al. 2017).
It has been successfully applied to measure MPs with the notable advantages of being more
efficient even with complex samples. However, the method is destructive and time consuming
(Dümichen et al. 2015).

382 3.4 Concerns about identification/quantification of MPs

Following the identification and quantification (sometimes by counting or weighing) of MPs 383 using the previously discussed procedures, the results are often presented in varying units. A 384 major concern is the lack of harmonization in the units of previous reports on the quantity of 385 MPs in sediment (Hanvey et al. 2017). As a way of checking if this trend has changed since 386 the Hanvey review, we conducted a search of the ISI web of knowledge database with the 387 keywords "sediment" and "microplastics", restricted to papers published in 2019. This revealed 388 that the inconsistency in result reporting remains a concern, although there are tentative 389 indications of a movement towards a consensus on the use of items or particles per kg of dried 390 391 sediment. A total of 38 publications met our search criteria and of these, only 7 quantified the measured MPs in terms of some form of units. Four of these reported the concentrations of 392 MPs in items or particles per kg or g dry sediment (Mu et al. 2019; Yuan et al. 2019; Zhang et 393 al. 2019); two reported as particles or items per kg (without specifying whether dry weight or 394 wet weight of sediment) (Bordós et al. 2019; Li et al. 2019), while the remaining study reported 395 as items/km of river (Xiong et al. 2019). It is recommended that items per kg be adopted as a 396 standard as some recent studies have further classified MPs into fibres, particles, fragments, 397

filaments, microbeads, foams etc. based on their shape (Bertoldi et al. 2021; Kumar et al. 2021;Sang et al. 2021). Also, the use of both weight and volume is recommended where possible.

Another concern from the foregoing is the cost and efficiency of the methods discussed above. 400 The need for "a cheaper, faster and more easily applied method" is glaring, especially if 401 402 sufficient data from lower income regions of the world are to be obtained in order to establish temporal and spatial trends on a global scale (Maes et al. 2017). One positive step in this 403 404 direction, as suggested by (Andrady 2011) is the use of lipophilic fluorescent dyes such as Nile Red to enhance visual identification/quantification of MPs under microscopes. Nile Red is a 405 406 solvatochromic fluorescent dye that fluoresces with varying emission spectrum depending on the polarity of its environment (Maes et al., 2017). It has been applied successfully to the 407 408 identification and quantification of microplastics in environmental samples (Nel et al. 2020; Maes et al., 2017, Erni-Cassola et al., 2017, Shim et al., 2016) and can cut analysis time down 409 410 by 30-58% compared to the analysis of unstained samples (Nel et al. 2021a). Overall, this approach in combination with fluorescence microscopy and image analysis software is -411 according to Erni-Cassola et al. (2017) - a fast, reliable and cost-effective method of detecting, 412 quantifying and sizing polyethylene (PE), polypropylene (PP), polystyrene (PS), and Nylon-6 413 particles in the size range of 20 µm to 1 mm. Shim et al. (2016) described the Nile Red staining 414 approach as "straight forward and quick for identifying/quantifying polymer particles in 415 laboratory-controlled samples" and reported a recovery rate of 98% for PE (100-300 µm). In 416 comparing the recovery rates of LDPE particles (in the size range of 100-300 µm) using the 417 Nile Red staining method and FTIR, Shim et al. (2016) reported $96\pm7\%$ for FTIR and $98\pm3\%$ 418 for the Nile Red method. Furthermore, the Nile Red method gave on average a 1.4 times higher 419 particle count than FTIR, following comparison of the quantitative analysis of field samples 420 using both methods (Shim et al., 2016). This shows that the fluorescent dye staining method, 421 which is a lot cheaper and faster, is also efficient. Despite its limitation of staining other non-422 plastic organic materials, it provides (among other advantages) a good solution to the difficulty 423 in visual identification of transparent and white MPs (Shim et al., 2016). It is also highly 424 unlikely that Nile Red would pose any risk of secondary contamination or interference with 425 further analysis of additives present in the MPs (e.g., phthalates or OPEs) (Ramirez et al. 2019). 426

427 3.5 Quality assurance/quality control (QA/QC)

428 Considering the ubiquity of MPs, it is extremely important to put measures in place to prevent 429 contamination of samples and ensure data accuracy. It is also important to guard against over-430 and under-estimation (Dekiff et al. 2014). The level of such accuracy largely depends on the

extent to which standard QA/QC measures are adhered to (Ibe and Kullenberg 1995). Rinsing 431 all apparatus 3 or 4 times with purified water (Wen et al. 2018, Jiang et al. 2018, Yuan et al. 432 2019b) and then cleaning the workspace with 70% alcohol (Wen et al, 2018) has been reported. 433 A strict use of 100% cotton lab coats as well as nitrile gloves, in addition to ensuring that all 434 equipment and glass containers are covered by aluminum foil has also been reported (Wang et 435 al., 2019). Some researchers pre-filter all liquids before use (Wang et al, 2019, Yuan et al 436 2019). Other quality assurance and quality control measures that are recommended include 437 validation studies and procedural blanks. Validation studies are laboratory tests performed to 438 439 verify that a technique or procedure is accurate and reproducible, specifically highlighting any limitations. Hanvey et al., (2017) reported that only 7 out of the 43 reviewed studies conducted 440 some form of validation test. Some more recent studies have used procedural blanks as QA/QC 441 measures (Wang et al., 2019; Yuan et al., 2019b, Jiang et al., 2018). Other steps that have been 442 undertaken in previous studies to ensure the integrity of the results of MPs studies, include the 443 use of non-plastic sampling, storage, and processing tools (Hanke et al. 2013). It is 444 recommended that publishers insist on proper QA/QC measures as a condition for publication 445 446 as this will ensure the integrity of reported data. Also, something similar to the work of Andrade et al., (2020) that proposed a minimum information for publication of IR-related data on MPs 447 characterization (Andrade et al., 2020) is strongly recommended for the study of MPs in 448 sediments. 449

450 3.6 Possible effect of MP extraction methods on the analysis of associated additives

The bioavailability of additives such as OPEs that are present in sediments, will very likely 451 vary substantially depending on whether they are sorbed to MPs or to naturally occurring 452 453 sediment organic matter. It is therefore important to be able to differentiate between OPEs bound to MPs present in sediment and those associated with the sediment itself. Moreover, in 454 order to achieve such differentiation, it is crucial to understand the impact exerted on the 455 determination of OPEs by the procedures used to isolate MPs from sediments - e.g. will the 456 use of Nile Red dye chemically affect OPEs and/or introduce chemical interferences? Although 457 not much has been done in freshwater environments, a few studies have looked at the presence 458 459 of plastic additives in MPs isolated from marine environments (see Fries et al. 2013; Hirai et al. 2011; Rani et al. 2015) each identified MP types and associated organic plastic additives 460 (OPAs) following their extraction from sediments using the density separation approach. 461 QA/QC measures such as the use of metal spoons, covering all materials with aluminium foil 462 after each step and rinsing of equipment with ultra-pure water were reported, but no mention 463

464 was made of the possible effect of MP extraction procedures on the analysis of OPEs associated 465 with MPs. In view of this, we have examined a cross section of recent studies on MP extraction 466 from sediments with a view to identifying possible sources of OPE contamination to isolated 467 MPs subsequently analyzed for these and/or related additives (Table 4). The table also presents 468 a cross section of techniques adopted by some researchers for identification and quantification 469 of MPs.

Table 4: Examples of procedures adopted to measure MPs in sediment and possible impacts on the analysis of OPEs and/or related MP additives.

Reference	Sampling method	Extraction method	Clean-up	Identification	QA/QC	Possible source of OPEs/other additives
(Wen et al. 2018)	A shovel was used to collect samples into aluminum foil and kept at 5 °C.	Density Separation	Digestion with 30% H ₂ O ₂ and Fe (II) solution (catalyst)	micro-Raman spectroscopy	The workspace was cleaned with 70% alcohol before. All pieces of apparatus were rinsed three times with distilled water and covered with aluminum foil. Blank tests were used.	No obvious source was identified but it is highly recommended that procedural blanks are incorporated as there is a possibility of contamination from indoor air.
(He et al. 2018; Liu o al. 2018; Zhou et al. 2018)	Clean stainless- steel shovels and spoons were used.	Air flotation and density separation using saturated sodium chloride solution	Use of 30% H ₂ O ₂ for 72 h at 50 °C was the most favored digestion method.	Visual identification under an optical microscope and confirmation of MPs using micro- Fourier transform infrared (µ-FT-IR) and Raman spectroscopy	All materials thoroughly cleaned and covered with aluminum foil. Lab coats always worn during analysis. Blank tests conducted for MPs.	All studies only used blanks to monitor background contamination by MPs. A total of 33 fibers were extracted from one of the blanks and another study excluded fibers from the study entirely as they acknowledged that atmospheric contamination of samples with fibers from the air was unavoidable.

Jiang et al., 2018	Sediment (0-2 cm) from lakeshore line was collected with a stainless- steel shovel.	Density separation was used	H ₂ O ₂ (30%, v/v) catalyzed with ferrous sulfate.	microscopic identification and Raman Spectroscopy	All equipment was pre-cleaned three times by ultrapure water and wrapped in aluminum foil when not in use. Blank tests were used to determine the background values of contamination of MPs from the laboratory	No obvious source was identified but it is strongly recommended procedural blanks be incorporated as there is a possibility of contamination from indoor air.
Wang et al., 2019	For surface sediments stainless- steel shovel was used. A plexiglass tube was used for vertical core.	Sediments were dried at 60 °C overnight. NaI solution used followed by sieving with a steel sieve The process was repeated three times.	30% H ₂ O ₂ and 65% HNO ₃ (1:3, v/v) for two days	FTIR analysis SEM	All liquids used were filtered with 0.45 µm membrane filters All glass containers were covered by aluminum foil, and a cotton laboratory coat and nitrile gloves were worn. Moreover, the entire process of analysis and identification was conducted by one person in a closed room, with blank experiments conducted to detect any ambient microplastic contamination	No obvious source was identified but it is highly recommended procedural blanks be incorporated as there is a possibility of contamination from indoor air.
(Yuan et al., 2019b)	Sediment was collected	A density separation was employed	Digestion using 30%	Visual identification as well as	Cleaning of tools with filtered pure water before sampling.	No obvious source was identified but it is highly recommended procedural

from boat	H ₂ O ₂	Stereoscopic and	Nitrile gloves and a cotton lab	blanks be incorporated as
using a Van	overnight.	Raman analyses	gown worn	there is a possibility of
Veen grab sampler	The digested	were employed for identification/	All solutions filtered through a	contamination from indoor air.
	diluted and	Quantification	Method blank tests were carried	
	filtered using a 0.45		out in the laboratory.	
	μm filter.		The experiment was repeated	
			three times.	

473 4. Temporal trends of MPs concentrations in freshwater sediment

Freshwater sediments may serve as long-term or temporary MP sinks (Ballent et al., 2016, 474 Corcoran et al., 2015, Nel et al., 2018). The first published study on MPs in lake sediments, 475 reported concentrations of $1,108 \pm 983$ particles/m² in beach sediments from the sub-alpine 476 Lake Garda in Italy (Imhof et al., 2013). MP contamination of lake sediments is now widely 477 documented (Carril-Ajuria et al. 2020; Gopinath et al. 2020; Hu et al. 2020; Tavşanoğlu et al. 478 2020). However, reliable data on temporal trends is scarce, with most studies reporting 479 480 concentrations from a single moment in time (Tavşanoğlu et al. 2020; Wu et al. 2020). In order to fill this data gap long-term studies designed to capture the temporal variations in MP 481 concentration are required. Additionally, sediment cores can be used to measure historical 482 temporal trends. Radiometrically-dated sediment cores have been used by Turner et al. (2019) 483 and Matsuguma et al., (2017) to investigate the historical change in MP concentrations 484 (Matsuguma et al. 2017; Turner et al. 2019). Matsuguma et al. (2017) analyzed dated sediment 485 cores collected from a range of water bodies (e.g., canals, lakes, coastal zones, harbors) from 486 Japan, Thailand, Malaysia, and South Africa. Results showed a clear increasing trend, with 487 higher MP concentrations found associated with more recent sediment layers. A correlation 488 between plastic production and MP concentration was observed within the Asian and African 489 samples. 490

Turner et al. (2019) traced the onset of MP pollution to the 1950s, which coincides with the period when large-scale production and use of plastics commenced. The Turner et al. (2019) study also reported a correlation between increased plastic fiber concentrations and global annual plastic production figures as well as reporting that identifiable concentrations of polystyrene emerged only after the onset of its production and use. These interesting correlations and trends pose questions as to whether similar trends can be identified with plastic additives.

498 5. Temporal trends of organophosphate esters in freshwater sediments

The occurrence of OPEs in sediments have been reported by several studies (Castro-Jiménez and Ratola 2020; Liao et al. 2020; Ren et al. 2019; Wang et al. 2018) and in one such study, $\sum OPE$ concentrations were lowest in the oldest sediment layers but increased gradually towards the more recent sediment layers. Although the sediments were not dated, there appears

to be some degree of correlation with the global production and usage of OPEs (Liao et al. 503 2020). Similarly, in a study that investigated the concentration of OPEs in sediment cores and 504 surface sediments from the Great Lakes, Cao et al. (2017) identified a possible correlation 505 between the trend in sediment deposition of OPEs and the production/regulation trend over the 506 period of interest. One good example of such a trend was the observed increase of the 507 concentration of OPEs in sediment core layers dated after 2000 which coincides with the period 508 during which worldwide production volume of OPEs tripled as a result of large-scale 509 replacement of PBDEs with OPEs in consumer goods (Iqbal et al. 2017). It was also observed 510 that the replacement of TCEP with TCIPP after the former was phased out, might be 511 responsible for the exponential increase in the concentration of TCIPP in more recent Great 512 Lakes sediment layers (Cao et al. 2017). The same study reported similar concentrations of 513 OPEs as those reported in sediment in other parts of the world such as China (Cao et al. 2012) 514 and Austria (Martínez-Carballo et al. 2007). Combined, such studies highlight increasing risks 515 516 of ecotoxicity because of environmental pollution with OPEs that is increasing at a similar rate to that of MPs. To illustrate, a study by Cho et al. (1996) has traced the increase in OPE 517 concentrations in a rural river (Kurose River, Japan) to the leaching of tri-cresyl phosphate 518 519 (TCP) isomers from agricultural plastic films.

520 7. Current research gaps and future perspectives

521 This review reveals increasing interest in the study of MPs in the freshwater environment and an urgent need to review the current trend in plastic production and work towards improved 522 523 recycling methods. This is particularly important because a consistency between the trend of MP abundance in the environment and the global trend of plastic production has been reported 524 (Matsuguma et al. 2017). In fact, Turner et al. (2019) reported a relatively low number of MPs 525 526 in older sediment cores compared to earlier ones. It is also important to extend understanding 527 of MP pollution to other parts of the world such as Africa, where only 12 studies appear to have been carried out between January 2000 and June 2021 notwithstanding the fact that some 528 529 of the world's largest freshwater bodies are in Africa.

530 It is also clear that there are several research gaps in the study of MPs, especially in freshwater531 environments (Table 2). Beyond the lack of standardized procedures in sediment sampling,

532 there is limited evidence of the comparability between the various sampling methods. This can

be addressed by investigating the possible differences between MP concentrations using thedifferent sampling methods in a controlled environment.

535 Research into effective MPs extraction and detection methods with focus on standardized measurement and reporting procedures is encouraged. Further development and 536 standardization of simple, cheap, high throughput and accurate methods like those based on 537 fluorescence dye staining is also recommended to facilitate relevant studies in low-income and 538 developing countries. Furthermore, international comparison and validation studies are 539 required to ascertain the quality of data provided, as well as the comparability of results from 540 541 different labs around the world. Development and production of laboratory standard reference materials for MPs in sediment is the ultimate aim for achieving a standardized QA/QC protocol 542 543 for MPs analysis in sediment.

The role of MPs as conduits of chemical pollutants, widely used as plastic additives, to the 544 freshwater environment is poorly understood. While there seems to be an apparent correlation 545 between concentrations of MPs and chemical pollution in the few studies that have addressed 546 this topic, it is not clear if MPs act as a source or a sink of lipophilic chemicals to the aquatic 547 environment. In particular, nothing is known about the partitioning of chemical plastics 548 additives in sediments between sediment particles and the MPs themselves. Thus, discerning 549 the impacts of MPs from those of the additives present, is an important research goal. Given 550 551 the potential implications of this for the bioavailability of such chemical additives, this is a significant research gap that should be addressed. Specifically, the impact on additive 552 553 bioavailability of several factors including the type of plastic polymer, the concentration and physicochemical properties of chemical additives, the organic content of sediment and the 554 555 temperature, is unknown. Studies are urgently required to understand the fate and behavior of hazardous chemical additives present in MPs and the factors influencing their release to the 556 557 freshwater environment. This also means that while working on biodegradable plastics and other ways of promoting "Reduction, Re-use and Recycling" of plastics; sources of MP 558 559 pollution and the use of chemical additives should be carefully considered because the facilitated degradation of these biodegradable plastics may provide a further source of chemical 560 pollution to the environment. 561

562 Finally, more studies on temporal/spatial trends of MPs (and associated additives such as 563 OPEs) in radiometrically-dated freshwater sediment cores are required, not only to provide information on historical trends but also to enable modelling and prediction of future trends and associated risks to the aquatic environment. This will also provide valuable information for shaping pollution control strategies and the effect of hydrodynamic conditions on the distribution of MPs in freshwater systems.

568

569 8.0 Conclusion

Following a critical review of the current state-of-knowledge on MPs in freshwater sediment, 570 certain trends such as increased interest in freshwater sediments as well as a consistency 571 between the trend of microplastic abundance in the environment and the global trend of plastic 572 production were observed and the need to work towards bridging research gaps in key areas 573 was highlighted. These research gaps include; developing and producing standard reference 574 materials for MPs in sediment, understanding the role of MPs as conduits of chemical 575 pollutants, understanding partitioning of chemical plastics additives in sediments between 576 577 sediment particles and the MPs themselves and the impact on additive bioavailability of several factors including the type of plastic polymer, the concentration and physicochemical properties 578 579 of chemical additives, the organic content of sediment and the temperature.

580 Methods for the analysis of MPs in freshwater sediment was reviewed and although no obvious 581 impact on the analysis of OPEs and/or related MP additives was seen, it is highly recommended 582 that QA/QC measures such as procedural blanks be taken to prevent secondary introduction of 583 some of the target plastic additives.

584

585 Declaration of competing interest

586 The authors declare that they have no known competing interests.

587

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592 Supporting Information.

- 593 Details including chemical names, structures, CAS numbers, molecular formulae, applications,
- 594 environmental/health hazards of OPEs are provided in the supporting information.

595 **REFERENCES**

- 596 Alomar, C., Estarellas, F. and Deudero, S., 2016. Microplastics in the Mediterranean Sea: dep-
- 597 osition in coastal shallow sediments, spatial variation and preferential grain size. Marine Envi-598 ronmental Research, 115, pp.1-10.
- 599 Altmann, K., Goedecke, C., Bannick, C.G., Abusafia, A., Steinmetz, H.S.C., Braun, U. and
- 600 Eichen, U., 2019, September. Identification and Quantification of Microplastic in Sewage sys-
- 601 tems by TED-GC-MS. In Proceedings of the 16th International Conference Environmental Sci-
- 602 ence and Technology, Rhodes, Greece (pp. 4-7).
- 603 Andrade, J.M., Ferreiro, B., López-Mahía, P. and Muniategui-Lorenzo, S., 2020. Standardi-
- 604 zation of the minimum information for publication of infrared-related data when microplas-
- 605 tics are characterized. Marine Pllution Bulletin, 154, p.111035.
- Andrady, A.L., 2011. Microplastics in the marine environment. Marine pollution bulletin, 607 62(8), pp.1596-1605.
- 608 Arthur, C., J. Baker and H. Bamford (eds). 2009. Proceedings of the International Research
- 609 Workshop on the Occurrence, Effects and Fate of Microplastic Marine Debris. Sept 9-11, 2008.
- 610 NOAA Technical Memorandum NOS-OR&R-30.Bakir A, Rowland SJ, Thompson RC. 2012.
- 611 Competitive sorption of persistent organic pollutants onto microplastics in the marine
- 612 environment. Marine Pollution Bulletin 64:2782-2789.
- Bakir, A., Rowland, S.J. and Thompson, R.C., 2012. Competitive sorption of persistent organic
 pollutants onto microplastics in the marine environment. Marine Pollution Bulletin, 64(12),
 pp.2782-2789.
- 616 Baldwin, A.K., Spanjer, A.R., Rosen, M.R. and Thom, T., 2020. Microplastics in Lake Mead 617 national recreation area, USA: occurrence and biological uptake. PloS one, 15(5), p.e0228896.
- 618 Ballent, A., Corcoran, P.L., Madden, O., Helm, P.A. and Longstaffe, F.J., 2016. Sources and
- 619 sinks of microplastics in Canadian Lake Ontario nearshore, tributary and beach sediments. Ma-620 rine Pollution Bulletin, 110(1), pp.383-395.
- 621 Barnes, D.K., Galgani, F., Thompson, R.C. and Barlaz, M., 2009. Accumulation and fragmen-
- 622 tation of plastic debris in global environments. Philosophical transactions of the royal society
- 623 B: Biological Sciences, 364(1526), pp.1985-1998.
- 624 Bertoldi, C., Lara, L.Z., Fernanda, A.D.L., Martins, F.C., Battisti, M.A., Hinrichs, R. and Fer-
- 625 nandes, A.N., 2021. First evidence of microplastic contamination in the freshwater of Lake
- 626 Guaíba, Porto Alegre, Brazil. Science of The Total Environment, 759, p.143503.
- 627 Besseling, E., Wegner, A., Foekema, E.M., Van Den Heuvel-Greve, M.J. and Koelmans, A.A.,
- 628 2013. Effects of microplastic on fitness and PCB bioaccumulation by the lugworm Arenicola
- 629 marina (L.). Environmental Science & Technology, 47(1), pp.593-600.

630 Boatman RJ, Corley RA, Green T, Klaunig JE, Udden MM. 2004. Review of studies 631 concerning the tumorigenicity of 2-butoxyethanol in b6c3f1 mice and its relevance for human

632 risk assessment. Journal of Toxicology and Environmental Health, Part B 7:385-398.

633 Bordós, G., Urbányi, B., Micsinai, A., Kriszt, B., Palotai, Z., Szabó, I., Hantosi, Z. and Szo-

634 boszlay, S., 2019. Identification of microplastics in fish ponds and natural freshwater environ-

635 ments of the Carpathian basin, Europe. Chemosphere, 216, pp.110-116.

Borrelle, S.B., Ringma, J., Law, K.L., Monnahan, C.C., Lebreton, L., McGivern, A., Murphy,
E., Jambeck, J., Leonard, G.H., Hilleary, M.A. and Eriksen, M., 2020. Predicted growth in
plastic waste exceeds efforts to mitigate plastic pollution. Science, 369(6510), pp.1515-1518.

639 Boucher J, Friot D. 2017. Primary microplastics in the oceans: A global evaluation of 640 sources:IUCN Gland, Switzerland. IUCN. Available at: 641 chttps://www.iven.org/content/primary_microplastics_courses_[Accessed 20 June 2021]

- 641 <https://www.iucn.org/content/primary-microplastics-oceans> [Accessed 30 June 2021].
- Bray, L., Digka, N., Tsangaris, C., Camedda, A., Gambaiani, D., de Lucia, G.A., Matiddi, M.,
- 643 Miaud, C., Palazzo, L., Pérez-del-Olmo, A. and Raga, J.A., 2019. Determining suitable fish to 644 monitor plastic ingestion trends in the Mediterranean Sea. Environmental pollution, 247,
- 645 pp.1071-1077.
- Browne, M.A., Crump, P., Niven, S.J., Teuten, E., Tonkin, A., Galloway, T. and Thompson,
 R., 2011. Accumulation of microplastic on shorelines woldwide: sources and sinks. Environmental science & technology, 45(21), pp.9175-9179.
- 649 Browne, M.A., Chapman, M.G., Thompson, R.C., Amaral Zettler, L.A., Jambeck, J. and Mal-650 los, N.J., 2015. Spatial and temporal patterns of stranded intertidal marine debris: is there a
- 651 picture of global change?. Environmental Science & Technology, 49(12), pp.7082-7094.
- 652 Cadogan D.F, Howick C.J 2000. Plasticizers.. [online] Techorg.polsl.pl. Available at: 653 <https://www.techorg.polsl.pl/images/pliki/Instrukcje/TChI_WOJP_Za%C5%82acznik_1.pdf 654 > [Accessed 5 July 2021].
- 655 Cao D, Guo J, Wang Y, Li Z, Liang K, Corcoran MB, et al. 2017. Organophosphate esters in 656 sediment of the great lakes. Environmental Science & Technology 51:1441-1449.
- Cao, S., Zeng, X., Song, H., Li, H., Yu, Z., Sheng, G. and Fu, J., 2012. Levels and distributions
 of organophosphate flame retardants and plasticizers in sediment from Taihu Lake, China. Environmental Toxicology and Chemistry, 31(7), pp.1478-1484.
- 660 Carril-Ajuria, L., Santos, M., Roldán-Romero, J.M., Rodriguez-Antona, C. and de Velasco, G.,
- 661 2020. Prognostic and predictive value of PBRM1 in clear cell renal cell carcinoma. Cancers,
 662 12(1), p.16.
- 663 Castro-Jiménez, J. and Ratola, N., 2020. An innovative approach for the simultaneous quanti-
- tative screening of organic plastic additives in complex matrices in marine coastal areas. Environmental Science and Pollution Research, 27(10), pp.11450-11457.
- 666 Cheung, P.K., Cheung, L.T.O. and Fok, L., 2016. Seasonal variation in the abundance of ma-
- 667 rine plastic debris in the estuary of a subtropical macro-scale drainage basin in South China.
- 668 Science of the Total Environment, 562, pp.658-665.
- 669 Cho KJ, Hirakawa T, Mukai T, Takimoto K, Okada M. 1996. Origin and stormwater runoff of 670 tcp (tricresyl phosphate) isomers. Water research 30:1431-1438.

- 671 Choong, W.S., Hadibarata, T. and Tang, D.K.H., 2021. Abundance and distribution of micro-
- 672 plastics in the water and riverbank sediment in Malaysia—A review. Biointerface Res. Appl.
- 673 Chem, 11, pp.11700-11712.
- 674 Chowdhury, G.W., Koldewey, H.J., Duncan, E., Napper, I.E., Niloy, M.N.H., Nelms, S.E.,
- 675 Sarker, S., Bhola, S. and Nishat, B., 2020. Plastic pollution in aquatic systems in Bangladesh:
- 676 A review of current knowledge. Science of the Total Environment, p.143285.
- Claessens, M., Van Cauwenberghe, L., Vandegehuchte, M.B. and Janssen, C.R., 2013. New
 techniques for the detection of microplastics in sediments and field collected organisms. Marine pollution bulletin, 70(1-2), pp.227-233.
- 680 Claessens, M., De Meester, S., Van Landuyt, L., De Clerck, K. and Janssen, C.R., 2011. Oc-
- currence and distribution of microplastics in marine sediments along the Belgian coast. Marine
 pollution bulletin, 62(10), pp.2199-2204.
- 683 Cole, M., 2013. Microplastic Swallowing Zooplankton Environ. Sci. Technol., 47, pp.6646-684 6655.
- 685 Corcoran PL, Norris T, Ceccanese T, Walzak MJ, Helm PA, Marvin CH. 2015. Hidden plastics
- 686 of lake ontario, canada and their potential preservation in the sediment record. Environmental
- 687 Pollution 204:17-25.
- Crew, A., Gregory-Eaves, I. and Ricciardi, A., 2020. Distribution, abundance, and diversity of
 microplastics in the upper St. Lawrence River. Environmental Pollution, 260, p.113994.
- 690 Crichton EM, Noël M, Gies EA, Ross PS. 2017. A novel, density-independent and ftir-
- 691 compatible approach for the rapid extraction of microplastics from aquatic sediments. 692 Analytical Methods 9:1419-1428.
- 693 Crawford CB, Quinn B. 2017. 10 microplastic identification techniques. In: Microplastic 694 pollutants, (Crawford CB, Quinn B, eds):Elsevier, 219-267.
- Dahms, H.T., van Rensburg, G.J. and Greenfield, R., 2020. The microplastic profile of an urbanAfrican stream. Science of The Total Environment, 731, p.138893.
- 697 Dekiff JH, Remy D, Klasmeier J, Fries E. 2014. Occurrence and spatial distribution of 698 microplastics in sediments from norderney. Environmental Pollution 186:248-256.
- Deng H, Wei R, Luo W, Hu L, Li B, Shi H. 2020. Microplastic pollution in water and sedimentin a textile industrial area. Environmental Pollution 258:113658.
- 701 Deng, Y., Zhang, Y., Qiao, R., Bonilla, M.M., Yang, X., Ren, H. and Lemos, B., 2018. Evi-
- 702 dence that microplastics aggravate the toxicity of organophosphorus flame retardants in mice
- 703 (Mus musculus). Journal of hazardous materials, 357, pp.348-354.
- do Sul, J.A.I. and Costa, M.F., 2014. The present and future of microplastic pollution in the marine environment. Environmental pollution, 185, pp.352-364.
- 706 Dovidat, L.C., Brinkmann, B.W., Vijver, M.G. and Bosker, T., 2020. Plastic particles adsorb
- 707 to the roots of freshwater vascular plant Spirodela polyrhiza but do not impair growth. Limnol-
- 708 ogy and Oceanography Letters, 5(1), pp.37-45.

- 709 Dümichen, E., Barthel, A.K., Braun, U., Bannick, C.G., Brand, K., Jekel, M. and Senz, R.,
- 710 2015. Analysis of polyethylene microplastics in environmental samples, using a thermal 711 decomposition method. Water research, 85, pp.451-457.
- 712 Dümichen, E., Eisentraut, P., Bannick, C.G., Barthel, A.K., Senz, R. and Braun, U., 2017. Fast
- 713 identification of microplastics in complex environmental samples by a thermal degradation
- 714 method. Chemosphere, 174, pp.572-584.
- Figessa, R., Nankabirwa, A., Basooma, R. and Nabwire, R., 2020. Occurrence, distribution and
 size relationships of plastic debris along shores and sediment of northern Lake Victoria. Environmental Pollution, 257, p.113442.
- 718 Elert, A.M., Becker, R., Duemichen, E., Eisentraut, P., Falkenhagen, J., Sturm, H. and Braun,719 U., 2017. Comparison of different methods for MP detection: what can we learn from them,
- 720 and why asking the right question before measurements matters?. Environmental Pollution,
- 721 231, pp.1256-1264.
- Eo, S., Hong, S.H., Song, Y.K., Han, G.M. and Shim, W.J., 2019. Spatiotemporal distribution
 and annual load of microplastics in the Nakdong River, South Korea. Water research, 160,
 pp.228-237.
- Friksen, M., Mason, S., Wilson, S., Box, C., Zellers, A., Edwards, W., Farley, H. and Amato,
 S., 2013. Microplastic pollution in the surface waters of the Laurentian Great Lakes. Marine
 pollution bulletin, 77(1-2), pp.177-182.
- 728 Erni-Cassola, G., Gibson, M.I., Thompson, R.C. and Christie-Oleza, J.A., 2017. Lost, but 729 found with Nile Red: a novel method for detecting and quantifying small microplastics (1 mm
- 730 to $20 \ \mu\text{m}$) in environmental samples. Environmental science & technology, 51(23), pp.13641-
- 731 13648.
- 732 EU. 2009. European community. European union risk assessment report, tris (2-chlorethyl)
- 733 phosphate, tcep. Cas-no.: 115-96-8, einecs-no.: 204-118-5. Final approved version.
- 734 Luxembourg: Office for official publications of the european communities; july 2009. Office
- 735 for Official Publications of the European Communities; July 2009.
- 736 Everaert, G., Van Cauwenberghe, L., De Rijcke, M., Koelmans, A.A., Mees, J., 737 Vandegehuchte, M. and Janssen, C.R., 2018. Risk assessment of microplastics in the ocean:
- Modelling approach and first conclusions. Environmental pollution, 242, pp.1930-1938.
- Field CB, Behrenfeld MJ, Randerson JT, Falkowski P. 1998. Primary production of thebiosphere: Integrating terrestrial and oceanic components. Science 281:237-240.
- 741 Fischer, E.K., Paglialonga, L., Czech, E. and Tamminga, M., 2016. Microplastic pollution in
- 742 lakes and lake shoreline sediments-a case study on Lake Bolsena and Lake Chiusi (central
- 743 Italy). Environmental pollution, 213, pp.648-657.
- Fischer, M. and Scholz-Böttcher, B.M., 2017. Simultaneous trace identification and quantification of common types of microplastics in environmental samples by pyrolysis-gas chroma-
- 746 tography-mass spectrometry. Environmental science & technology, 51(9), pp.5052-5060.
- 747 Fries E, Dekiff JH, Willmeyer J, Nuelle M-T, Ebert M, Remy D. 2013. Identification of 748 polymer types and additives in marine microplastic particles using pyrolysis-gc/ms and 749 scanning electron microscopy. Environmental Science: Processes & Impacts 15:1949-1956.

- Fuller S, Gautam A. 2016. A procedure for measuring microplastics using pressurized fluidextraction. Environmental science & technology 50:5774-5780.
- 752 Garcia-Garin, O., Vighi, M., Sala, B., Aguilar, A., Tsangaris, C., Digka, N., Kaberi, H., Eljar-
- 753 rat, E. and Borrell, A., 2020. Assessment of organophosphate flame retardants in Mediterra-
- nean Boops boops and their relationship to anthropization levels and microplastic ingestion.
- 755 Chemosphere, 252, p.126569.
- 756 Geyer, R., Jambeck, J.R. and Law, K.L., 2017. Production, use, and fate of all plastics ever 757 made. Science advances, 3(7), p.e1700782.
- 758 Gopinath, K., Seshachalam, S., Neelavannan, K., Anburaj, V., Rachel, M., Ravi, S., Bharath,
- 759 M. and Achyuthan, H., 2020. Quantification of microplastic in red hills lake of Chennai city,
- 760 Tamil Nadu, India. Environmental Science and Pollution Research, 27(26), pp.33297-33306.
- 761 Guimarães ATB, Charlie-Silva I, Malafaia G. 2021. Toxic effects of naturally-aged 762 microplastics on zebrafish juveniles: A more realistic approach to plastic pollution in 763 freshwater ecosystems. Journal of Hazardous Materials 407:124833.
- 764 Galgani, F., Hanke, G., Werner, S., Oosterbaan, L., Nilsson, P., Fleet, D., Kinsey, S., Thomp-
- son, R.C., Van Franeker, J., Vlachogianni, T. and Scoullos, M., 2013. Guidance on Monitoring
- 766 of Marine Litter in European Seas: A Guidance Document Within the Common Implementa-
- 767 tion Strategy for the Marine Strategy Framework Directive. Publications Office of the Euro-
- 768 pean Union, Luxembourg.
- 769 Hanvey, J.S., Lewis, P.J., Lavers, J.L., Crosbie, N.D., Pozo, K. and Clarke, B.O., 2017. A
- review of analytical techniques for quantifying microplastics in sediments. Analytical Meth-771 ods, 9(9), pp.1369-1383.
- 772 Hartmann, N.B., Huffer, T., Thompson, R.C., Hassellöv, M., Verschoor, A., Daugaard, A.E.,
- 773 Rist, S., Karlsson, T., Brennholt, N., Cole, M. and Herrling, M.P., 2019. Are we speaking the
- same language? Recommendations for a definition and categorization framework for plastic
- 775 debris.
- Hawley, G.G. and Lewis, R.J (2001). Hawley's Condensed Chemical Dictionary 14th Edition.John Wiley & Sons, Inc. New York, NY, pp. 472,927 ISBN: 9780471387350
- He D, Luo Y, Lu S, Liu M, Song Y, Lei L. 2018. Microplastics in soils: Analytical methods,
 pollution characteristics and ecological risks. TrAC Trends in Analytical Chemistry 109:163-
- 780 172. 781 Herdenderf C = 1082 Large lakes of the world Journal of Great Lakes Research 8(3)
- Herdendorf, C.E., 1982. Large lakes of the world. Journal of Great Lakes Research, 8(3),pp.379-412.
- Herrera M, Matuschek G, Kettrup A. 2003. Fast identification of polymer additives by
 pyrolysis-gas chromatography/mass spectrometry. Journal of analytical and applied pyrolysis
 70:35-42.
- Hidalgo-Ruz, V., Gutow, L., Thompson, R.C. and Thiel, M., 2012. Microplastics in the marine
 environment: a review of the methods used for identification and quantification. Environmental
 science & technology, 46(6), pp.3060-3075.
- Hirai, H., Takada, H., Ogata, Y., Yamashita, R., Mizukawa, K., Saha, M., Kwan, C., Moore,C., Gray, H., Laursen, D. and Zettler, E.R., 2011. Organic micropollutants in marine plastics

- debris from the open ocean and remote and urban beaches. Marine pollution bulletin, 62(8),pp.1683-1692.
- Hoellein, T., Rojas, M., Pink, A., Gasior, J. and Kelly, J., 2014. Anthropogenic litter in urban freshwater ecosystems: distribution and microbial interactions. PloS one, 9(6), p.e98485.
- 795 Hoffman K, Gearhart-Serna L, Lorber M, Webster TF, Stapleton HM. 2017. Estimated tris(1,3-
- 796 dichloro-2-propyl) phosphate exposure levels for U.S. Infants suggest potential health risks.
- 797 Environmental Science & Technology Letters 4:334-338.
- Hoffman MJ, Hittinger E. 2017. Inventory and transport of plastic debris in the laurentian greatlakes. Marine pollution bulletin 115:273-281.
- 800 Horton AA, Svendsen C, Williams RJ, Spurgeon DJ, Lahive E. 2017 Large microplastic 801 particles in sediments of tributaries of the river thames, uk-abundance, sources and methods
- 802 for effective quantification. Marine pollution bulletin 114:218-226.
- 803 Hou R, Xu Y, Wang Z. 2016. Review of OPFRs in animals and humans: Absorption, 804 bioaccumulation, metabolism, and internal exposure research. Chemosphere 153:78-90.
- Hu, D., Zhang, Y. and Shen, M., 2020. Investigation on microplastic pollution of DongtingLake and its affiliated rivers. Marine Pollution Bulletin, 160, p.111555.
- Hurley, R.R., Woodward, J.C. and Rothwell, J.J., 2017. Ingestion of microplastics by freshwater tubifex worms. Environmental science & technology, 51(21), pp.12844-12851.
- 809 Ibe AC, Kullenberg G. 1995. Quality assurance/quality control (qa/qc) regime in marine 810 pollution monitoring programmes: The gipme perspective. Marine Pollution Bulletin 31:209-811 213.
- 812 Imhof HK, Schmid J, Niessner R, Ivleva NP, Laforsch C. 2012. A novel, highly efficient 813 method for the separation and quantification of plastic particles in sediments of aquatic 814 environments. Limnology and oceanography: methods 10:524-537.
- 815 Imhof, H.K., Ivleva, N.P., Schmid, J., Niessner, R. and Laforsch, C., 2013. Contamination of
 816 beach sediments of a subalpine lake with microplastic particles. Current biology, 23(19),
 817 pp.R867-R868.
- 818 Iqbal, M., Syed, J.H., Katsoyiannis, A., Malik, R.N., Farooqi, A., Butt, A., Li, J., Zhang, G.,
- 819 Cincinelli, A. and Jones, K.C., 2017. Legacy and emerging flame retardants (FRs) in the fresh-820 water ecosystem: A review. Environmental research, 152, pp.26-42.
- Jian, M., Zhang, Y., Yang, W., Zhou, L., Liu, S. and Xu, E.G., 2020. Occurrence and distribution of microplastics in China's largest freshwater lake system. Chemosphere, 261, p.128186.
- 823 Jiang, C., Yin, L., Wen, X., Du, C., Wu, L., Long, Y., Liu, Y., Ma, Y., Yin, Q., Zhou, Z. and
- Pan, H., 2018. Microplastics in sediment and surface water of west dongting lake and south
 dongting lake: abundance, source and composition. International journal of environmental resource and public health 15(10) p 2164
- search and public health, 15(10), p.2164.
- 827 Kalčíková, G., Gotvajn, A.Ž., Kladnik, A. and Jemec, A., 2017. Impact of polyethylene mi-
- crobeads on the floating freshwater plant duckweed Lemna minor. Environmental Pollution,
 230, pp.1108-1115.

- 830 Käppler, A., Fischer, D., Oberbeckmann, S., Schernewski, G., Labrenz, M., Eichhorn, K.J. and
- 831 Voit, B., 2016. Analysis of environmental microplastics by vibrational microspectroscopy:
- FTIR, Raman or both?. Analytical and bioanalytical chemistry, 408(29), pp.8377-8391.
- 833 Käppler, A., Fischer, M., Scholz-Böttcher, B.M., Oberbeckmann, S., Labrenz, M., Fischer, D.,
- 834 Eichhorn, K.J. and Voit, B., 2018. Comparison of μ-ATR-FTIR spectroscopy and py-GCMS
- 835 as identification tools for microplastic particles and fibers isolated from river sediments. Ana-
- 836 lytical and bioanalytical chemistry, 410(21), pp.5313-5327.
- Karami, A., Golieskardi, A., Ho, Y.B., Larat, V. and Salamatinia, B., 2017. Microplastics in
 eviscerated flesh and excised organs of dried fish. Scientific reports, 7(1), pp.1-9.
- 839 Karlsson, T.M., Vethaak, A.D., Almroth, B.C., Ariese, F., van Velzen, M., Hassellöv, M. and
- 840 Leslie, H.A., 2017. Screening for microplastics in sediment, water, marine invertebrates and
- 841 fish: method development and microplastic accumulation. Marine pollution bulletin, 122(1-2),
- 842 pp.403-408.
- Kawagoshi Y, Nakamura S, Fukunaga I. 2002. Degradation of organophosphoric esters inleachate from a sea-based solid waste disposal site. Chemosphere 48:219-225.
- Kedzierski, M., Le Tilly, V., Bourseau, P., Bellegou, H., César, G., Sire, O. and Bruzaud, S.,
 2016. Microplastics elutriation from sandy sediments: a granulometric approach. Marine pollution bulletin, 107(1), pp.315-323.
- Klein, S., Dimzon, I.K., Eubeler, J. and Knepper, T.P., 2018. Analysis, occurrence, and degradation of microplastics in the aqueous environment. In Freshwater microplastics (pp. 51-67).
 Springer, Cham.
- 851 Koelmans, A.A., Besseling, E., Wegner, A. and Foekema, E.M., 2013. Plastic as a carrier of
- 852 POPs to aquatic organisms: a model analysis. Environmental science & technology, 47(14),
- 853 pp.7812-7820.
- Kumar R, Sharma P, Bandyopadhyay S. 2021. Evidence of microplastics in wetlands:
 Extraction and quantification in freshwater and coastal ecosystems. Journal of Water Process
 Engineering 40:101966.
- Lai, S., Xie, Z., Song, T., Tang, J., Zhang, Y., Mi, W., Peng, J., Zhao, Y., Zou, S. and
 Ebinghaus, R., 2015. Occurrence and dry deposition of organophosphate esters in atmospheric
 particles over the northern South China Sea. Chemosphere, 127, pp.195-200.
- 860 Lee, K.W., Shim, W.J., Kwon, O.Y. and Kang, J.H., 2013. Size-dependent effects of micro 861 polystyrene particles in the marine copepod Tigriopus japonicus. Environmental science &
- 862 technology, 47(19), pp.11278-11283.
- 863 Lenz R, Enders K, Stedmon CA, Mackenzie DM, Nielsen TG. 2015. A critical assessment of 864 visual identification of marine microplastic using raman spectroscopy for analysis 865 improvement. Marine Pollution Bulletin 100:82-91.
- 866 Li R, Zhang L, Xue B, Wang Y. 2019. Abundance and characteristics of microplastics in the
- 867 mangrove sediment of the semi-enclosed maowei sea of the south china sea: New implications
- 868 for location, rhizosphere, and sediment compositions. Environmental Pollution 244:685-692.

- Liao, C., Kim, U.J. and Kannan, K., 2020. Occurrence and distribution of organophosphate esters in sediment from northern Chinese coastal waters. Science of The Total Environment,
- 871 704, p.135328.
- 872 Liu, M., Lu, S., Song, Y., Lei, L., Hu, J., Lv, W., Zhou, W., Cao, C., Shi, H., Yang, X. and He,
- 873 D., 2018. Microplastic and mesoplastic pollution in farmland soils in suburbs of Shanghai,
- 874 China. Environmental Pollution, 242, pp.855-862.
- 875 Löder MGJ, Kuczera M, Mintenig S, Lorenz C, Gerdts G. 2015. Focal plane array detector-876 based micro-fourier-transform infrared imaging for the analysis of microplastics in 877 environmental samples. Environmental Chemistry 12:563-581.
- Maes T, Jessop R, Wellner N, Haupt K, Mayes AG. 2017. A rapid-screening approach to detectand quantify microplastics based on fluorescent tagging with nile red. Sci Rep-Uk 7.
- 880 Magni, S., Gagné, F., André, C., Della Torre, C., Auclair, J., Hanana, H., Parenti, C.C., Bona-
- 881 soro, F. and Binelli, A., 2018. Evaluation of uptake and chronic toxicity of virgin polystyrene
- 882 microbeads in freshwater zebra mussel Dreissena polymorpha (Mollusca: Bivalvia). Science
- 883 of the Total Environment, 631, pp.778-788.
- Mai, L., Bao, L.J., Shi, L., Wong, C.S. and Zeng, E.Y., 2018. A review of methods for measuring microplastics in aquatic environments. Environmental Science and Pollution Research,
 25(12), pp.11319-11332.
- Mani T, Primpke S, Lorenz C, Gerdts G, Burkhardt-Holm P. 2019. Microplastic pollution in
 benthic midstream sediments of the rhine river. Environmental science & technology 53:60536062.
- 890 Martínez-Carballo, E., González-Barreiro, C., Sitka, A., Scharf, S. and Gans, O., 2007. Deter-
- 891 mination of selected organophosphate esters in the aquatic environment of Austria. Science of
- 892 the total environment, 388(1-3), pp.290-299.
- 893 Mason, S.A., Kammin, L., Eriksen, M., Aleid, G., Wilson, S., Box, C., Williamson, N. and 894 Riley, A., 2016. Pelagic plastic pollution within the surface waters of Lake Michigan, USA.
- 895 Journal of Great Lakes Research, 42(4), pp.753-759.
- 896 Masura, J., Baker, J., Foster, G. and Arthur, C., 2015. Laboratory Methods for the Analysis of
- 897 Microplastics in the Marine Environment: Recommendations for quantifying synthetic parti-898 cles in waters and sediments.
- 899 Matsuguma, Y., Takada, H., Kumata, H., Kanke, H., Sakurai, S., Suzuki, T., Itoh, M., Okazaki,
- 900 Y., Boonyatumanond, R., Zakaria, M.P. and Weerts, S., 2017. Microplastics in sediment cores
- 901 from Asia and Africa as indicators of temporal trends in plastic pollution. Archives of environ-
- 902 mental contamination and toxicology, 73(2), pp.230-239.
- Mattsson, K., Johnson, E.V., Malmendal, A., Linse, S., Hansson, L.A. and Cedervall, T., 2017.
 Brain damage and behavioural disorders in fish induced by plastic nanoparticles delivered
 through the food chain. Scientific reports, 7(1), pp.1-7.
- 906 McGoran, A.R., Clark, P.F. and Morritt, D.J.E.P., 2017. Presence of microplastic in the diges-
- 907 tive tracts of European flounder, Platichthys flesus, and European smelt, Osmerus eperlanus,
- 908 from the River Thames. Environmental Pollution, 220, pp.744-751.

- 909 Mu, J., Qu, L., Jin, F., Zhang, S., Fang, C., Ma, X., Zhang, W., Huo, C., Cong, Y. and Wang,
- 910 J., 2019. Abundance and distribution of microplastics in the surface sediments from the north-911 ern Bering and Chukchi Seas. Environmental Pollution, 245, pp.122-130.
- Murray, F. and Cowie, P.R., 2011. Plastic contamination in the decapod crustacean Nephrops
 norvegicus (Linnaeus, 1758). Marine pollution bulletin, 62(6), pp.1207-1217.
- 914 Nel, H.A., Dalu, T. and Wasserman, R.J., 2018. Sinks and sources: Assessing microplastic
- 915 abundance in river sediment and deposit feeders in an Austral temperate urban river system.
- 916 Science of the Total Environment, 612, pp.950-956.
- 917 Nel, H.A., Smith, G.H.S., Harmer, R., Sykes, R., Schneidewind, U., Lynch, I. and Krause, S.,
- 918 2020. Citizen science reveals microplastic hotspots within tidal estuaries and the remote Scilly919 Islands, United Kingdom. Marine Pollution Bulletin, 161, p.111776.
 - 920 Nel, H.A., Chetwynd, A.J., Kelleher, L., Lynch, I., Mansfield, I., Margenat, H., Onoja, S., Op-
 - 921 penheimer, P.G., Smith, G.H.S. and Krause, S., 2021. Detection limits are central to improve
 - 922 reporting standards when using Nile red for microplastic quantification. Chemosphere, 263,
- 923 p.127953.
- 924 Nel, H.A., Chetwynd, A.J., Kelly, C.A., Stark, C., Valsami-Jones, E., Krause, S. and Lynch, I.,
- 925 2021. An Untargeted Thermogravimetric Analysis-Fourier Transform Infrared-Gas Chroma-
- 926 tography-Mass Spectrometry Approach for Plastic Polymer Identification. Environmental Sci-927 ence & Technology.
- 928 Ng, K.L. and Obbard, J.P., 2006. Prevalence of microplastics in Singapore's coastal marine 929 environment. Marine pollution bulletin, 52(7), pp.761-767.
- 930 Nuelle M-T, Dekiff JH, Remy D, Fries E. 2014. A new analytical approach for monitoring931 microplastics in marine sediments. Environmental Pollution 184:161-169.
- 932 Oliviero, M., Tato, T., Schiavo, S., Fernández, V., Manzo, S. and Beiras, R., 2019. Leachates
- 933 of micronized plastic toys provoke embryotoxic effects upon sea urchin Paracentrotus lividus.
- 934 Environmental Pollution, 247, pp.706-715.
- 935 Oni, B.A., Ayeni, A.O., Agboola, O., Oguntade, T. and Obanla, O., 2020. Comparing micro936 plastics contaminants in (dry and raining) seasons for Ox-Bow Lake in Yenagoa, Nigeria. Eco937 toxicology and environmental safety, 198, p.110656.
- Pagter, E., Frias, J., Kavanagh, F. and Nash, R., 2020. Varying levels of microplastics in benthic sediments within a shallow coastal embayment. Estuarine, Coastal and Shelf Science, 243,
 p.106915.
- Parker, B., Andreou, D., Green, I.D. and Britton, J.R., 2021. Microplastics in freshwater fishes:
 Occurrence, impacts and future perspectives. Fish and Fisheries, 22(3), pp.467-488.
- 943 Pan, Z., Guo, H., Chen, H., Wang, S., Sun, X., Zou, Q., Zhang, Y., Lin, H., Cai, S. and Huang,
- 944 J., 2019. Microplastics in the Northwestern Pacific: Abundance, distribution, and characteris-
- 945 tics. Science of the Total Environment, 650, pp.1913-1922.
- 946 Pantelaki I, Voutsa D. 2019. Organophosphate flame retardants (OPFRs): A review on
- 947 analytical methods and occurrence in wastewater and aquatic environment. Science of The 948 Total Environment 649:247-263.

- 949 Peller JR, Eberhardt L, Clark R, Nelson C, Kostelnik E, Iceman C. 2019. Tracking the
- distribution of microfiber pollution in a southern lake michigan watershed through the analysisof water, sediment and air. Environmental Science: Processes & Impacts 21:1549-1559.
- 952 Peng, G., Zhu, B., Yang, D., Su, L., Shi, H. and Li, D., 2017. Microplastics in sediments of the
- 953 Changjiang Estuary, China. Environmental Pollution, 225, pp.283-290.
- 954 Peng G, Xu P, Zhu B, Bai M, Li D. 2018. Microplastics in freshwater river sediments in 955 shanghai, china: A case study of risk assessment in mega-cities. Environmental Pollution 956 234:448-456.
- Prata, J.C., da Costa, J.P., Duarte, A.C. and Rocha-Santos, T., 2019. Methods for sampling and
 detection of microplastics in water and sediment: A critical review. TrAC Trends in Analytical
 Chemistry, 110, pp.150-159.
- 960 Qiu Q, Tan Z, Wang J, Peng J, Li M, Zhan Z. 2016. Extraction, enumeration and identification
- 961 methods for monitoring microplastics in the environment. Estuarine, Coastal and Shelf Science 962 176:102-109.
- 963 Quinn B, Murphy F, Ewins C. 2017. Validation of density separation for the rapid recovery of964 microplastics from sediment. Analytical Methods 9:1491-1498.
- 965 Ramírez-Álvarez, N., Mendoza, L.M.R., Macías-Zamora, J.V., Oregel-Vázquez, L., Alvarez-
- 966 Aguilar, A., Hernández-Guzmán, F.A., Sánchez-Osorio, J.L., Moore, C.J., Silva-Jiménez, H.
- 967 and Navarro-Olache, L.F., 2020. Microplastics: Sources and distribution in surface waters and
- 968 sediments of Todos Santos Bay, Mexico. Science of the Total Environment, 703, p.134838.
- 969 Ramirez MMB, Caamal RD, von Osten JR. 2019. Occurrence and seasonal distribution of 970 microplastics and phthalates in sediments from the urban channel of the ria and coast of 971 campeche, mexico. Science of the Total Environment 672:97-105.
- 972 Rani, M., Shim, W.J., Han, G.M., Jang, M., Al-Odaini, N.A., Song, Y.K. and Hong, S.H., 2015.
- 973 Qualitative analysis of additives in plastic marine debris and its new products. Archives of 974 environmental contamination and toxicology, 69(3), pp.352-366.
- 975 Reemtsma, T., Quintana, J.B., Rodil, R., Garcı, M. and Rodrı, I., 2008. Organophosphorus 976 flame retardants and plasticizers in water and air I. Occurrence and fate. TrAC Trends in 977 Analytical Chemistry, 27: 727-737.
- 878 Ren, G., Chu, X., Zhang, J., Zheng, K., Zhou, X., Zeng, X. and Yu, Z., 2019. Organophosphate
 979 esters in the water, sediments, surface soils, and tree bark surrounding a manufacturing plant
 980 in north China. Environmental Pollution, 246, pp.374-380.
- 981 Rochman, C.M., Browne, M.A., Halpern, B.S., Hentschel, B.T., Hoh, E., Karapanagioti, H.K.,
- 982 Rios-Mendoza, L.M., Takada, H., Teh, S. and Thompson, R.C., 2013. Classify plastic waste as
- 983 hazardous. Nature, 494(7436), pp.169-171.
- Rochman, C.M., Hoh, E., Kurobe, T. and Teh, S.J., 2013b. Ingested plastic transfers hazardous
 chemicals to fish and induces hepatic stress. Scientific reports, 3(1), pp.1-7.
- 986 Rodrigues, M.O., Abrantes, N., Gonçalves, F.J.M., Nogueira, H., Marques, J.C. and Gonçalves,
- 987 A.M.M., 2018. Spatial and temporal distribution of microplastics in water and sediments of a
- 988 freshwater system (Antuã River, Portugal). Science of the total environment, 633, pp.1549-
- 989 1559.

- 990 Sanchez, W., Bender, C. and Porcher, J.M., 2014. Wild gudgeons (Gobio gobio) from French
- rivers are contaminated by microplastics: preliminary study and first evidence. Environmentalresearch, 128, pp.98-100..
- 993 Sang, W., Chen, Z., Mei, L., Hao, S., Zhan, C., bin Zhang, W., Li, M. and Liu, J., 2021. The 994 abundance and characteristics of microplastics in rainwater pipelines in Wuhan, China. Science
- 995 of The Total Environment, 755, p.142606.
- 996 Scherer, C., Weber, A., Lambert, S. and Wagner, M., 2018. Interactions of microplastics with 997 freshwater biota. In Freshwater microplastics (pp. 153-180). Springer, Cham.
- 998 Scherer, C., Weber, A., Stock, F., Vurusic, S., Egerci, H., Kochleus, C., Arendt, N., Foeldi, C.,
- 999 Dierkes, G., Wagner, M. and Brennholt, N., 2020. Comparative assessment of microplastics in 1000 water and sediment of a large European river. Science of The Total Environment, 738, 1001 p.139866.
- Schessl M, Johns C, Ashpole S. 2019. Microbeads in sediment, dreissenid mussels, and anuransin the littoral zone of the upper St. Lawrence river, New York. Pollution 5:41-52.
- 1004 Shi, Q., Wang, M., Shi, F., Yang, L., Guo, Y., Feng, C., Liu, J. and Zhou, B., 2018. Develop-1005 mental neurotoxicity of triphenyl phosphate in zebrafish larvae. Aquatic Toxicology, 203, 1006 pp.80-87.
- 1007 Shim, W.J., Song, Y.K., Hong, S.H. and Jang, M., 2016. Identification and quantification of 1008 microplastics using Nile Red staining. Marine pollution bulletin, 113(1-2), pp.469-476.
- 1009 Shim, W.J., Hong, S.H. and Eo, S.E., 2017. Identification methods in microplastic analysis: a 1010 review. Analytical methods, 9(9), pp.1384-1391.
- 1011 Shruti, V.C., Jonathan, M.P., Rodriguez-Espinosa, P.F. and Rodríguez-González, F., 2019. Mi-
- 1012 croplastics in freshwater sediments of Atoyac River basin, Puebla city, Mexico. Science of the
- 1013 Total Environment, 654, pp.154-163.
- 1014 Sigmaaldrich.com. 2021. Organophosphate ester and phthalate ester metabolites in urine from
- primiparas in Shenzhen, China: Implications for health risks. | Sigma-Aldrich. [online] Available at: https://www.sigmaaldrich.com/GB/en/tech-docs/paper/1245313 [Accessed 6 July
 2021].
- 1018 Silva-Cavalcanti, J.S., Silva, J.D.B., de França, E.J., de Araújo, M.C.B. and Gusmao, F., 2017.
- 1019 Microplastics ingestion by a common tropical freshwater fishing resource. Environmental pol-1020 lution, 221, pp.218-226.
- Song, Y.K., Hong, S.H., Jang, M., Han, G.M., Rani, M., Lee, J. and Shim, W.J., 2015. A com-parison of microscopic and spectroscopic identification methods for analysis of microplastics
- 1023 in environmental samples. Marine pollution bulletin, 93(1-2), pp.202-209.
- 1024 Stapleton, H.M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J.D., Blum, A. and Webster, T.F., 1025 2009. Detection of organophosphate flame retardants in furniture foam and US house dust.
- 1026 Environmental science & technology, 43(19), pp.7490-7495.
- 1027 Stolte A, Forster S, Gerdts G, Schubert H. 2015. Microplastic concentrations in beach 1028 sediments along the german baltic coast. Marine Pollution Bulletin 99:216-229.
- Su, L., Xue, Y., Li, L., Yang, D., Kolandhasamy, P., Li, D. and Shi, H., 2016. Microplastics intaihu lake, China. Environmental Pollution, 216, pp.711-719.

1031 Tavşanoğlu ÜN, Kankılıç GB, Akca G, Çırak T, Erdoğan Ş. 2020. Microplastics in a dam lake

1032 in turkey: Type, mesh size effect, and bacterial biofilm communities. Environmental Science 1033 and Pollution Research 27:45688-45698.

1034 Teuten, E.L., Saquing, J.M., Knappe, D.R., Barlaz, M.A., Jonsson, S., Björn, A., Rowland, 1035 S.J., Thompson, R.C., Galloway, T.S., Yamashita, R. and Ochi, D., 2009. Transport and release

1036 of chemicals from plastics to the environment and to wildlife. Philosophical transactions of the

1037 royal society B: biological sciences, 364(1526), pp.2027-2045.

1038 Toumi H, Abidli S, Bejaoui M. 2019. Microplastics in freshwater environment: The first
1039 evaluation in sediments from seven water streams surrounding the lagoon of bizerte (northern
1040 tunisia). Environmental Science and Pollution Research 26:14673-14682.

1041 Turner, A., Wallerstein, C. and Arnold, R., 2019. Identification, origin and characteristics of

bio-bead microplastics from beaches in Western Europe. Science of The Total Environment,664, pp.938-947.

1044 Turner, S., Horton, A.A., Rose, N.L. and Hall, C., 2019. A temporal sediment record of micro-1045 plastics in an urban lake, London, UK. Journal of Paleolimnology, 61(4), pp.449-462.

1046 Van Cauwenberghe, L., Claessens, M., Vandegehuchte, M.B. and Janssen, C.R., 2015. Micro1047 plastics are taken up by mussels (Mytilus edulis) and lugworms (Arenicola marina) living in
1048 natural habitats. Environmental pollution, 199, pp.10-17.

1049 Van der Veen I, de Boer J. 2012. Phosphorus flame retardants: Properties, production,1050 environmental occurrence, toxicity and analysis. Chemosphere 88:1119-1153.

1051 Vaughan, R., Turner, S.D. and Rose, N.L., 2017. Microplastics in the sediments of a UK urban1052 lake. Environmental Pollution, 229, pp.10-18.

1053 Verne J. 1998. Twenty thousand leagues under the sea:Oxford University Press. ISBN:1054 9780198818649

1055 Vianello, A., Boldrin, A., Guerriero, P., Moschino, V., Rella, R., Sturaro, A. and Da Ros, L.,
1056 2013. Microplastic particles in sediments of Lagoon of Venice, Italy: First observations on
1057 occurrence, spatial patterns and identification. Estuarine, Coastal and Shelf Science, 130,
1058 pp.54-61.

1059 Wang FC-Y. 2000. Polymer additive analysis by pyrolysis–gas chromatography: I. Plasticizers.1060 Journal of Chromatography A 883:199-210.

1061 Wang, W., Ndungu, A.W., Li, Z. and Wang, J., 2017. Microplastics pollution in inland fresh1062 waters of China: a case study in urban surface waters of Wuhan, China. Science of the Total
1063 Environment, 575, pp.1369-1374.

1064 Wang J, Wang M, Ru S, Liu X. 2019. High levels of microplastic pollution in the sediments1065 and benthic organisms of the south yellow sea, china. Science of the Total Environment1066 651:1661-1669.

1067 Wang X, Zhu L, Zhong W, Yang L. 2018. Partition and source identification of 1068 organophosphate esters in the water and sediment of taihu lake, china. Journal of hazardous 1069 materials 360:43-50. 1070 Wang, Z., Qin, Y., Li, W., Yang, W., Meng, Q. and Yang, J., 2019. Microplastic contamination 1071 in freshwater: first observation in lake ulansuhai, yellow river basin, China. Environmental

- 1072 Chemistry Letters, 17(4), pp.1821-1830.
- 1073 Wei, G.L., Li, D.Q., Zhuo, M.N., Liao, Y.S., Xie, Z.Y., Guo, T.L., Li, J.J., Zhang, S.Y. and
- 1074 Liang, Z.Q., 2015. Organophosphorus flame retardants and plasticizers: sources, occurrence,
- 1075 toxicity and human exposure. Environmental Pollution, 196, pp.29-46.
- 1076 Wen, X., Du, C., Xu, P., Zeng, G., Huang, D., Yin, L., Yin, Q., Hu, L., Wan, J., Zhang, J. and 1077 Tan, S., 2018. Microplastic pollution in surface sediments of urban water areas in Changsha,
- 1078 China: abundance, composition, surface textures. Marine pollution bulletin, 136, pp.414-423.
- 1079 Wessel, C.C., Lockridge, G.R., Battiste, D. and Cebrian, J., 2016. Abundance and characteris-
- 1080 tics of microplastics in beach sediments: insights into microplastic accumulation in northern
- 1081 Gulf of Mexico estuaries. Marine Pollution Bulletin, 109(1), pp.178-183.
- 1082 Wilkens JL, McQueen AD, LeMonte JJ, Suedel BC. 2020. Initial survey of microplastics in
- 1083 bottom sediments from united states waterways. Bulletin of environmental contamination and
- 1084 toxicology 104:15-20.
- 1085 WHO. 1993. Environmental health criteria 140. Polychlorinated biphenyls and Terphenyls:79-1086 221.
- 1087 Woodall, L.C., Sanchez-Vidal, A., Canals, M., Paterson, G.L., Coppock, R., Sleight, V.,
- 1088 Calafat, A., Rogers, A.D., Narayanaswamy, B.E. and Thompson, R.C., 2014. The deep sea is 1089 a major sink for microplastic debris. Royal Society open science, 1(4), p.140317.
- Woodall, L.C., Gwinnett, C., Packer, M., Thompson, R.C., Robinson, L.F. and Paterson, G.L.,
 2015. Using a forensic science approach to minimize environmental contamination and to identify microfibres in marine sediments. Marine pollution bulletin, 95(1), pp.40-46.
- 1092 uty microfibres in marine sediments. Marine pollution bulletin, 95(1), pp.40-46.
- Wu, P., Tang, Y., Dang, M., Wang, S., Jin, H., Liu, Y., Jing, H., Zheng, C., Yi, S. and Cai, Z.,
 2020. Spatial-temporal distribution of microplastics in surface water and sediments of
 Maozhou River within Guangdong-Hong Kong-Macao Greater Bay Area. Science of the total
 environment, 717, p.135187.
- 1097 Xiong X, Wu C, Elser JJ, Mei Z, Hao Y. 2019. Occurrence and fate of microplastic debris in 1098 middle and lower reaches of the yangtze river–from inland to the sea. Science of the Total 1099 Environment 659:66-73.
- 1100 Xu, Q., Xing, R., Sun, M., Gao, Y. and An, L., 2020. Microplastics in sediments from an in-1101 terconnected river-estuary region. Science of The Total Environment, 729, p.139025.
- 1102 Yiying J, Huan L, Mahar RB, Zhiyu W, Yongfeng N. 2009. Combined alkaline and ultrasonic
- 1103 pretreatment of sludge before aerobic digestion. Journal of Environmental Sciences 21:279-1104 284.
- 1105 Yuan W, Liu X, Wang W, Di M, Wang J. 2019. Microplastic abundance, distribution and 1106 composition in water, sediments, and wild fish from poyang lake, china. Ecotoxicology and 1107 Environmental Safety 170:180-187.
- 1108 Zbyszewski, M. and Corcoran, P.L., 2011. Distribution and degradation of fresh water plastic 1109 particles along the beaches of Lake Huron, Canada. Water, Air, & Soil Pollution, 220(1), 1110 pp.365-372.

- 1111 Zbyszewski M, Corcoran PL, Hockin A. 2014. Comparison of the distribution and degradation
- of plastic debris along shorelines of the Great Lakes, North America. Journal of Great LakesResearch 40:288-299.
- 1114 Zeng X, Wu Y, Liu Z, Gao S, Yu Z. 2018. Occurrence and distribution of organophosphate
- 1115 ester flame retardants in indoor dust and their potential health exposure risk. Environmental
- 1116 toxicology and chemistry 37:345-352.
- 1117 Zhang C, Zhou H, Cui Y, Wang C, Li Y, Zhang D. 2019. Microplastics in offshore sediment1118 in the yellow sea and east china sea, china. Environmental pollution 244:827-833.
- 1119 Zhou, Q., Zhang, H., Fu, C., Zhou, Y., Dai, Z., Li, Y., Tu, C. and Luo, Y., 2018. The distribu-
- 1120 tion and morphology of microplastics in coastal soils adjacent to the Bohai Sea and the Yellow
- 1121 Sea. Geoderma, 322, pp.201-208.
- 1122 Zhu X. 2015. Optimization of elutriation device for filtration of microplastic particles from
- 1123 sediment. Marine Pollution Bulletin 92:69-72.
- 1124