

## Microplastic-Toxic Chemical Interaction: a Review Study on Quantified Levels, Mechanism and Implication

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### Abstract

Current problem facing researchers globally is microplastics as well as toxic chemical pollution of the ecosystem. Microplastics carry toxic chemicals in the ecosystem, serving as a vector for transport. In this study, a review of the literature has been conducted with the following objectives: (1) to summarise the concentrations of toxic chemicals such as heavy metals and hydrophobic organic contaminants sorbed on microplastics; (2) to evaluate their spatial distribution regarding adsorbed contaminant; (3) to discuss plausible mechanism by which microplastics adsorb or desorb toxic chemicals in the environment; (4) to discuss implications of their occurrence in air, water and soil media; and (5) to discuss the impact of ingested microplastics to human health. Microplastics are ubiquitous environmental contaminants. Concentrations of sorbed toxic chemicals varied with location which represents a local problem; industrialized areas (especially areas experiencing crude oil related activities or have history of crude oil pollution) have higher concentrations than less industrialized areas. Ingestion of microplastics has been demonstrated in a range of marine and soil organisms as well as edible plants, thus possibly contaminating the base of the food-web. Potential health effects to humans are by particle localization, chemical toxicity and microbial toxins. We conclude by highlighting the gap in knowledge and suggesting key future areas of research for scientists and policymakers.

**Keyword:** Air pollution, Micropollutants, Plastic debris, Risks, Soil pollution, Toxicity, Water pollution

### List of abbreviations

Polypropylene (PP), Polycarbonate (PC), expanded polystyrene (PS-E), polyarylsulfone (PSU), polystyrene (PS), thermoplastic elastomers (TPE), polyethylene terephthalate (PET), poly methyl methacrylate (PMMA), polyvinylchloride (PVC), polypropylene (PP), polyamides (PA), polyurethane (PUR), atomic fluorescence spectroscopy (AFS), inductively coupled plasma mass spectrophotometer (ICP-MS), inductively coupled plasma-optical emission spectrometry (ICP-OES); Flame Atomic Absorption Spectrometry (FAAS), field-portable-x-ray fluorescence (FP-XRF), capillary gas chromatograph equipped with electron capture detector and mass detector (cGC-ECD-MD), gas chromatograph equipped with electron capture detector (GC-ECD), liquid scintillation counting (LSC), gas chromatography-ion-trap mass spectrometers (GC-ITMS), liquid chromatography system coupled to a quadrupole linear ion trap tandem mass spectrometer (QqLIT-MS/MS); potentially toxic substances (PoTSs), decabromo diphenyl ether (BDE209), hexachlorocyclohexane isomers (HCHs), Polycyclic aromatic hydrocarbons (PAHs), Organochlorine Pesticides (OCPs), Dichlorodiphenyltrichloroethane and related compounds (DDTs), Dichlorodiphenyldichloroethylene (DDE), Polybrominated diphenyl ethers (PBDEs), Perfluorinated compounds (PFCs), polystyrene carboxylate (PS-COOH), perfluoroalkyl substances (PFASs), Bisphenol A (BPA), Octylphenols (OPs) and Nonylphenols (NPs), Brunauer-Emmett-Teller (BET), pseudo-first-order (PFO), pseudo-second-order (PSO), pore-volume diffusion model (PVDM), pore-volume and surface diffusion model (PVSDM), film-pore mass transfer (FPMT), surface microlayer (SML), quorum sensing (QS), scanning electron microscopy (SEM), Fourier-transform infrared (FT-IR), Scanning electron microscopy with energy-dispersive x-ray spectroscopy (SEM-EDS), X-ray diffraction (XRD), International Agency for Research on Cancer (IARC), internal mass transfer (IMT), external mass transfer (EMT); bioaccumulation/concentration factors (BCF), reactive oxygen species (ROS).

## 1. Introduction

Worldwide population continues to experience annual growth at an average rate of 1.68 % between the years 1955 to 2015. World population was near 370 million, at the end of the Great Famine of 1315–1317 and the Black Death in 1350 (Jean-Noël, 1980), now population have reached 7.7 billion people as of April 2019 revealing tremendous increase (Worldometer, 2019). This tremendous increase has brought with it an increase in the amount of waste generated by people. On-the-go lifestyles require easily disposable products, such as soda cans or bottles of water, but the accumulation of these products has led to increasing amounts of plastic pollution around the world (Figure 1b).

Plastic is an organic polymer synthesized from fossil feedstocks such as natural gas, oil or coal. In modern times, the first plastic manufactured was in 1907 called “Bakelite”. Due to the many benefits of plastics such as it’s cheap, versatile, lightweight and resistant, its worldwide production which was only 0.35 million metric ton in 1950, has increased nearly 200-fold, reaching 348 million metric tons in 2017 (Verla et. al., 2019a), with average annual growth of 9 % (Figure 1a). In 2017 alone, about 34.8 million metric tons of plastics end up in the marine environment. Overall, approximately 80 % of the plastics polluting the marine environment come from land-based sources (Browne et. al., 2008).

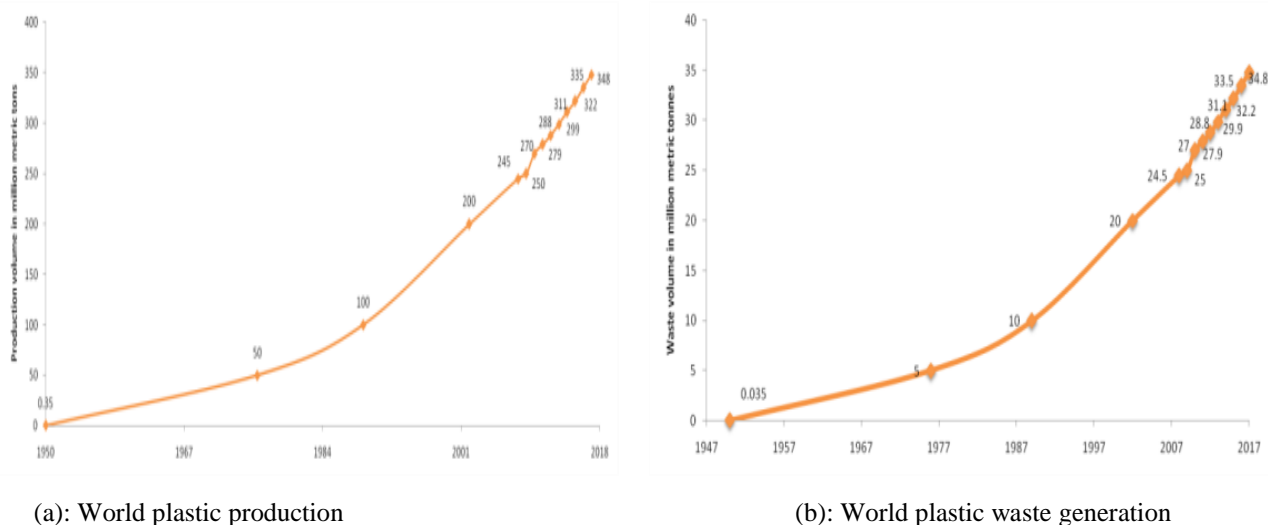


Figure 1: World plastic production and generated waste from 1950-2017 (Data source: Statista, 2008)

Plastics are comprised of two major category viz thermoplastics and thermosets. The former, thermoplastics are a family of plastics that are reversible and whose form can be easily altered by altering temperatures e.g polypropylene (PP), polycarbonate (PC), expanded polystyrene (PS-E), polyarylsulfone (PSU), polystyrene (PS), thermoplastic elastomers (TPE), polyethylene terephthalate (PET), poly methyl methacrylate (PMMA), polyvinyl-chloride (PVC), polypropylene (PP), polyamides (PA) and flouropolymer etc, which are more common in the environment. However, thermosets are family of plastics that cannot be reversed when heated. They undergo a chemical change creating a three dimensional network making them rigid e.g epoxy resins, vinyl ester, polyurethane (PUR), urea – formaldehyde, acrylic resin, silicone, melamine resin, phenolic resins, phenol – formaldehyde and unsaturated polyester etc. Polluting plastics are biochemically inert due to their large molecule size and can potentially cause great harm to the environment. Additionally, they can persist long time in the environment and can be accumulated in open oceans, sedimentary habitats, soil and plant tissues (Hirai et. al., 2011; Heskett et. al., 2012; Zhu et. al., 2019; Enyoh et. al., 2019).

Large plastic (macroplastic) debris in the environment undergoes degradation by natural processes to form tiny plastic fragments called microplastics. Apart from the natural microplastic formation, it can also be formed by anthropogenic means. Their sources vary including cosmetics, clothing, and industrial processes via urban wastewater treatment as well as nurdles etc. In last 2 decade, the problem they create in the environment has caused a shift of attention by environmental analytical researchers from macroplastics pollution to microplastics. It is an

emerging area of concern. Therefore, concern regarding plastic pollution has focused on sources, fate and ecological effects of microplastic particles in the environment (Cole et al., 2015; Hall et al., 2015; Rocha-Santos and Duarte, 2015; Enyoh et al., 2019).

Microplastics can be defined as plastic materials of micro size dimension (often between the range of 1  $\mu\text{m}$  – 5 mm) (Enyoh et al., 2019). Their presence in the environment is continually increasing particularly in ocean as observed by the increase in the frequency and quantity of plastic ingested by seabirds (Day et al., 1985; Boerger et al., 2010; Davison and Asch, 2011) and have recently been quantified in large quantity in soil ecosystem (reviewed by Zhu et al., 2019) and in plant tissues (Li et al., 2019; Enyoh et al., 2019). Microplastics were included as a priority descriptor (10; Marine Litter) in the Marine Strategy Framework Directive (MSFD) (Marine Litter) due to their impact in the marine environment (Directive 2008/56/EC, European Parliament and the Council, 2008). One of the primary environmental risks associated with microplastics is that they are ubiquitous and bioavailable for injection by marine organisms (Wright et al., 2013; Desforges et al., 2015), soil organisms (Lei et al. 2018; Kokalj et al., 2018; Zhu et al. 2018b; 2018c; Ju et al. 2019) and plant growing on microplastic polluted soils (Enyoh et al., 2019). Studies have reported their presence in sea animals such as seabirds, fish, sandhoppers, sea turtle, crustacean and mussel (Browne et al., 2008; Cole et al., 2011; Murray and Cowie, 2011; Ugolini et al., 2013; Foekema et al., 2013), soil invertebrates such as collembolan, oligochaeta (e.g. earthworms) and isopods (Lei et al. 2018; Kokalj et al., 2018; Zhu et al. 2018b; 2018c; Ju et al. 2019) and in plants such as wheat plants (Li et al., 2019). Furthermore, their presence in table salts, potable water and human excreta has also been reported (Karami et al., 2017; BBC, 2018). The health implication of their presence in animals is by blocking their digestive system and thus may lead to death of the animal or affect their feeding habit. However, in human, their health implication is yet to be ascertained but plausible effects include lung inflammation as well as primary and secondary genotoxicity (Wright and Kelly, 2017; Gasperi et al., 2018).

Microplastics have been reported to be in tandem with other toxic chemicals serving a vector for their transports in the environment. These toxic chemicals by adsorption processes attach to microplastics in the environment and may get injected through inhalation or contact. Then by desorption processes, they are released post-ingestion with potential for toxicity and / or accumulation in the food chain. Studies by Carpenter et al., (1972a,b) and Gregory, (1978) reported organic pollutant (viz polychlorinated biphenyls, PCBs) levels on marine plastic resin pellets; adsorbed either from plasticizers (commonly used before 1970s) or from ambient seawater. This behavior of microplastics interacting with toxic chemicals can be problematic for the environment because adverse effects of these toxic chemicals have been associated with mutagenic, teratogenic and carcinogenic effects (Verla et al., 2019c). Examples of toxic chemicals that have been reported include heavy metals such as iron (Fe), manganese (Mn), aluminium (Al), lead (Pb), copper (Cu), silver (Ag), zinc (Zn) and hydrophobic organic contaminants (HOCs) also referred to as persistent organic pollutants (POP) such as polyaromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). In this study, we presented a review of toxic chemicals (heavy metals and organic pollutants) concentrations on reported on microplastics found in the environment and animal, provide their possible adsorption and desorption (release) mechanism and the implications of their interaction to man and his environment.

## 2. Microplastics and toxic chemicals

The surface area to volume ratio of microplastics is large, making them a good sorbent for toxic chemicals such as heavy metals and organic chemicals i.e POPs loading on its surface. Therefore, acts as a conveyor of contaminants to organisms and between environment media. Generally, quantification of toxic chemicals from microplastic surface is mostly done using spectroscopic techniques following weak acid (e.g 10%  $\text{HNO}_3$ ) extraction for toxic metals while soxhlet assisted n-hexane, methanol (MeOH) or dichloromethane (DCM) extraction for organic pollutants. Concentrations are often reported in  $\mu\text{g/g}$  or  $\text{mg/kg}$  and  $\text{ng/g}$ . However, extraction chemical used is based on the type of microplastic. For example, methanol (MeOH) was reported to not be efficient for PCBs, DDE and nonylphenol extraction from marine PP pellets (Mato et al., 2001), which maybe efficient for PE or PVC etc. Some useful spectroscopic techniques for quantification of toxic chemicals after extraction have been reviewed in a recent study (Verla et al., 2019a). Summarily, the extractant and instrument for analysis, concentrations, types of toxic chemicals and study location reported in literature on microplastic is presented in Table 1.

Table 1: Reported contaminant concentrations in microplastic particles collected in the marine environment.

Toxic chemical	Specific contaminant	Extractant, instrument used	Concentrations	Location	References
<b>Halogen †</b>	Bromine (Br)	No extractant required/ Direct on dry microplastics, FP-XRF	6.6 – 4980	Woolacombe, South west, England	Massos and Turner, 2017
		No extractant required/ Direct on dry microplastics, FP-XRF	4 – 13300	Whitsand bay, South west, England	Massos and Turner, 2017
	Aluminum (Al)	Aqua regia, ICP-OES Aqua regia, ICP-MS	16.9 – 55.8 10 – 100	South west, England San Diego Bay, USA	Holmes et. al., 2012 Rochman et. al., 2014
	Arsenic (As)	Aqua regia, AFS Nitric acid, ICP-MS	0.35–2.89 0.000 - 0.008	Farms, China Maidao, Huangdao and Baian (China)	Mohsen et. al., 2019 Gao et. al., 2019
	Cadmium (Cd)	HF+HNO <sub>3</sub> +H <sub>2</sub> SO <sub>4</sub> , ICP- MS	2.16-17.56	Beijiang River, China	Wang et. al., 2017
		No extractant required, FP- XRF	38-1980	Whitsand bay, South west, England	Massos and Turner, 2017
		Aqua regia, ICP-MS	Nd-0.1	San Diego Bay, USA	Rochman et. al., 2014
		Direct on dry microplastics, FP-XRF	39-3390	Woolacombe, South west, England	Massos and Turner, 2017
		HF+HNO <sub>3</sub> +H <sub>2</sub> SO <sub>4</sub> , ICP- MS	2.16-17.56	Beijiang River, China	Wang et. al., 2017
		No extractant required, FP- XRF	38-1980	Whitsand bay, South west, England	Massos and Turner, 2017
		Nitric acid, AAS	0.37 – 1.77, 930 <sup>a</sup>	British Columbia, Canada	Munier and Bendell, 2018
		Nitric acid, ICP-MS	0.000 - 0.023	Maidao, Huangdao and Baian (China)	Gao et. al., 2019
	Chromium (Cr)	Aqua regia, ICP-MS	44 – 430	South west, England	Holmes et. al., 2012
		Aqua regia, ICP-MS	0.1 – 1	San Diego Bay, USA	Rochman et. al., 2014
		Aqua regia, ICP-MS Nitric acid, ICP-MS	4.43 - 37.47 0.000 - 0.003	Farm, China Maidao, Huangdao and Baian (China)	Mohsen et. al., 2019 Gao et. al., 2019
	Cobalt (Co)	Aqua regia, ICP-MS	17.7 – 107	South west, England	Holmes et. al., 2012
	Copper (Cu)	Aqua regia, ICP-MS	0.064 – 1.32	South west, England	Holmes et. al., 2012
		Aqua regia, FAAS	800 – 3000	n.a/lab study	Brennecke et. al., 2016
		HF+HNO <sub>3</sub> +H <sub>2</sub> SO <sub>4</sub> , ICP- MS	80.9 – 500.60	Beijiang River, China	Wang et. al., 2017
		Nitric acid, AAS	2.93 - 47.53, 188 <sup>a</sup>	British Columbia, Canada	Munier and Bendell, 2018
		Aqua regia, ICP-MS	1.37–21.67	Farms, China	Mohsen et. al., 2019
		Nitric acid, ICP-MS	0.079 - 0.223	Maidao, Huangdao and Baian (China)	Gao et. al., 2019
<b>Toxic metals †</b>	Iron (Fe)	Aqua regia, ICP-OES	41 – 97.8	South west, England	Holmes et. al., 2012
	Manganese (Mn)	Aqua regia, ICP-OES	1.16 – 20.5	South west, England	Holmes et. al., 2012
		Aqua regia, ICP-MS	10 – 100	San Diego Bay, USA	Rochman et. al., 2014
		Aqua regia, ICP-MS Nitric acid, ICP-MS	7.57–98.35 3.040 - 11.848	Farms, China Maidao, Huangdao and Baian (China)	Mohsen et. al., 2019 Gao et. al., 2019
	Nickel (Ni)	Aqua regia, ICP-MS	40 – 131	South west, England	Holmes et. al., 2012
		Aqua regia, ICP-MS	0.01 – 1	San Diego Bay, USA	Rochman et. al., 2014
HF+HNO <sub>3</sub> +H <sub>2</sub> SO <sub>4</sub> , ICP-		0.54 – 2.39	Beijiang River, China	Wang et. al., 2017	

	MS				
	Aqua regia, ICP-MS	1.31–43.2	Farms, China	Mohsen et. al., 2019	
Lead (Pb)	Nitric acid, AAS	0.71 - 17.68, 698000 <sup>a</sup>	British Columbia, Canada	Munier and Bendell, 2018	
	Aqua regia, ICP-MS	0.1 – 1	San Diego Bay, USA	Rochman et. al., 2014	
	No extractant required, FP-XRF	12-4820	Woolacombe, South west, England	Massos and Turner, 2017	
	HF+HNO <sub>3</sub> +H <sub>2</sub> SO <sub>4</sub> , ICP-MS	38.24 – 131.11	Beijiang River, China	Wang et. al., 2017	
	No extractant required, FP-XRF	17-1660	Whitsand bay, South west, England	Massos and Turner, 2017	
	Aqua regia, ICP-MS	2.56–40.8	Farms, China	Mohsen et. al., 2019	
	Nitric acid, ICP-MS	0.028 - 0.144	Maidao, Huangdao and Baian (China)	Gao et. al., 2019	
Titanium (Ti)	HF+HNO <sub>3</sub> +H <sub>2</sub> SO <sub>4</sub> , ICP-MS	13617.0 – 38823.7	Beijiang River, China	Wang et. al., 2017	
Zinc (Zn)	Nitric acid, ICP-OES	0.1-0.37	n.a/lab study	Hodson et. al., 2012	
	Aqua regia, ICP-MS	0.299 – 23.3	South west, England	Holmes et. al., 2012	
	Aqua regia, ICP-MS	1 – 10	San Diego Bay, USA	Rochman et. al., 2014	
	Aqua regia, FAAS	100 – 1000	n.a/ lab study	Brennecke et. al., 2016	
	HF+HNO <sub>3</sub> +H <sub>2</sub> SO <sub>4</sub> , ICP-MS	2414.8 – 11284.9	Beijiang River, China	Wang et. al., 2017	
	Nitric acid, AAS	4.3 - 604.24, 6667 <sup>a</sup>	British Columbia, Canada	Munier and Bendell, 2018	
	Aqua regia, ICP-MS	16.44–1190	Farms, China	Mohsen et. al., 2019	
	Nitric acid, ICP-MS	0 - 0.121	Maidao, Huangdao and Baian (China)	Gao et. al., 2019	
<b>Organic pollutants</b> <sup>tt</sup>	Hexane, GC	5000	Southern New England	Carpenter et. al., 1972b	
	Not specified, GC	< 100 – 4000	New Zealand	Gregory et al. 1978; Solly and Shanks 1976	
	ΣPCBs	Hexane/DCM, CGC-ECD-MD	97 – 117	Coastal sites in Japan	Mato et. al., 2001
		n-hexane/DCM, GC-ECD	5 – 18700	Tokyo, Japan	Endo et. al, 2005
		DCM, GCMS	<0.05-730	California, USA	Rios et. al., 2007
		DCM, GCMS	< 0.05 – 980	Hawaii	Rios et. al. 2007
		DCM, GCMS	< 0.05	Laysan albatross colon from Guadalupe Island, Mexico	Rios et. al. 2007
	DCM, GCMS	< 0.05	Los Angeles, USA (industrial site)	Rios et. al. 2007	
	Hexane, GC-ITMS	3590 – 10125	Kato Achaia, Greece	Karapanagioti et. al., 2009	
	n-hexane and methylene chloride (1:1, v/v), GC-ECD	243–491	(from seabird) Southern Brazil	Colabuono et. al., 2010	
		0.02 - 15.56	Portugal	Fries et. al., 2010	
	Hexane/DCM, GC-ITMS	1 – 78	Central pacific gyre,	Hirai et. al., 2011	
	Hexane/DCM, GC-ITMS	14	Pacific Ocean	Hirai et. al. 2011	
	Hexane/DCM, GC-ITMS	1-28	Caribbean Sea	Hirai et. al. 2011	
	Hexane/DCM, GC-ITMS	2-436	Kugenuma, Kanagawa	Hirai et. al. 2011	
Hexane/DCM, GC-ITMS	15-399	Los Angeles, USA	Hirai et. al. 2011		
Hexane/DCM, GC-ITMS	3-102	Thinh Long, Tonking Bay, Vietnam	Hirai et. al. 2011		
Hexane/DCM, GC-ITMS	2-285	Odaiba, Tokyo, Japan	Hirai et. al. 2011		
Hexane/DCM, GC-ITMS	1-61	Marbella Beach, Costa Rica	Hirai et. al. 2011		

	Hexane, GC-ITMS	0.1-9.9	Remote islands in the Pacific, Atlantic, Indian Oceans and the Caribbean Sea	Heskett et. al. 2012
	Hexane, GCMS	41 -113 (Year: 1989); 27 – 61 (Year 2008)	South African coastal waters (West Coast Park, Port Elizabeth and Woody Cape)	Ryan et. al., 2012
	Hexane, GCMS	3.8 – 42	North to South of San Diego County, California, USA	Van et. al., 2012
	Methanol ,LSC	600 – 6100 <sup>b</sup>	n.a/lab study	Teuten et. al., 2007
	DCM, GCMS	<0.05-6200	California, USA	Rios et. al., 2007
	DCM, GCMS	< 0.05 – 500	Hawaii	Rios et. al. 2007
	DCM, GCMS	640	Laysan albatross colon from Guadalupe Island, Mexico	Rios et. al. 2007
	DCM, GCMS	39 – 12000	Los Angeles, USA (industrial site)	Rios et. al. 2007
	Hexane, GC-ITMS	66 – 637	Kato Achaia, Greece	Karapanagioti et. al., 2009
ΣPAHs		0.2 - 319.2	Portuguese beaches	Fries et. al., 2010
	Hexane/DCM , GCMS	12-868	Central pacific gyre, Pacific Ocean	Hirai et. al., 2011
	Hexane/DCM , GCMS	112	Pacific Ocean	Hirai et. al. 2011
	Hexane/DCM , GCMS	88-105	Caribbean Sea	Hirai et. al. 2011
	Hexane/DCM , GCMS	0-9297	Kugenuma, Kanagawa	Hirai et. al. 2011
	Hexane/DCM , GCMS	39-656	Los Angeles, USA	Hirai et. al. 2011
	Hexane/DCM , GCMS	73-2024	Northern Vietnam	Hirai et. al. 2011
	Hexane/DCM , GCMS	58-521	Odaiba, Tokyo, Japan	Hirai et. al. 2011
	Hexane/DCM , GCMS	1-284	Marbella Beach, Costa Rica	Hirai et. al. 2011
	Hexane/DCM , GCMS	18-210	North to South of San Diego County, California, USA	Van et. al., 2012
	Hexane, GCMS	637 – 1996	São Paulo, Brazil	Fisner et al., 2013
	Hexane, GCMS	9.3-24000	9 coast in Portugal (Porto, Aveiro, Leiria, Alcobaça, Peniche, Cascais , Lisboa , Sines, Aljezur),	Mizukawa et al. 2013
	n-Hexane, GCMS	24400 – 164900	International pellet watch; 75 locations across America, Asia, Africa, Europe and Australia	Yeo et. al., 2017
Σ DDTs (DDT, DDD and DDE)	Hexane/DCM, CGC-ECD-MD	0.16 - 3.1	Coastal sites in Japan	Mato et. al., 2001
	Hexane/DCM , GC-ECD	1.69 – 276	International pellet watch; 30 locations across (North America, Europe, Asia, Africa and Oceania	Ogata et al. 2009
	Hexane, GC-ECD; GC-ITMS (for DDE only)	4.2 – 91.8	Kato Achaia, Greece	Karapanagioti et. al., 2009
	n-hexane and methylene chloride (1:1, v/v), GC-ECD	64.4–87.7	(from seabird) Southern Brazil	Colabuono et. al., 2010
	Hexane, GC-ITMS	0.7 - 4.1	Remote islands in the Pacific, Atlantic, Indian Oceans and the Caribbean Sea	Heskett et. al. 2012
ΣHCHs (αHCH, βHCH, γHCH, σHCH)	Hexane, GC-ECD	1.02 - 1.65	Kato Achaia, Greece	Karapanagioti et. al., 2009
	Hexane, GC- ECD	0.2–19.3	Remote islands in the Pacific, Atlantic, Indian	Heskett et. al. 2012

			Oceans and the Caribbean Sea	
Chlordane	n-hexane and methylene chloride (1:1, v/v), GC-ECD	4.29-14.4	(from seabird) Southern Brazil	Colabuono et. al., 2010
Cyclodienes	n-hexane and methylene chloride (1:1, v/v), GC-ECD	2.41 - 50.9	(from seabird) Southern Brazil	Colabuono et. al., 2010
Mirex	n-hexane and methylene chloride (1:1, v/v), GC-ECD	6.48 - 14.6	(from seabird) Southern Brazil	Colabuono et. al., 2010
hexachlorobenzene	n-hexane and methylene chloride (1:1, v/v), GC-ECD	12.4 - 17.5	(from seabird) Southern Brazil	Colabuono et. al., 2010
Hopanes	Hexane, GCMS	8300 - 62000	9 coast in Portugal (Porto, Aveiro, Leiria, Alcobaça, Peniche, Cascais , Lisboa , Sines, Aljezur),	Mizukawa et al. 2013
	n-Hexane, GCMS	1700 – 101000	International pellet watch; 75 locations across America, Asia, Africa, Europe and Australia	Yeo et. al., 2017
ΣPBDEs	Hexane/DCM , GC-IMTS	0.3 – 9909	Central pacific gyre,	Hirai et. al., 2011
	Hexane/DCM , GC-IMTS	6.2	Pacific Ocean	Hirai et. al. 2011
	Hexane/DCM , GC-IMTS	6.2 – 15.7	Caribbean Sea	Hirai et. al. 2011
	Hexane/DCM , GC-IMTS	0.8 – 136	Kugenuma, Kanagawa	Hirai et. al. 2011
	Hexane/DCM , GC-IMTS	5.3 - 41.4	Los Angeles, USA	Hirai et. al. 2011
	Hexane/DCM , GC-IMTS	0.3 – 412	Northern Vietnam	Hirai et. al. 2011
	Hexane/DCM , GC-IMTS	1.1 – 43.5	Odaiba, Tokyo, Japan	Hirai et. al. 2011
	Hexane/DCM , GC-IMTS	0.5 – 180	Marbella Beach, Costa Rica	Hirai et. al. 2011
ΣPFCs/ PFASs	Methanol, QqLIT-MS/MS	0.01 - 0.18	Corfu Island, Lavrio beach, Kato Achaia beach, Leros Island and Loutropyrgos beach in Greece	Llorca et. al., 2014
Aliphatic hydrocarbons	DCM, GCMS	50-330	California, USA	Rios et. al., 2007
	DCM, GCMS	0 – 8600	Los Angeles, USA (industrial site)	Rios et. al. 2007
BPA	n-Hexane, GCMS	<1 - 729.9	Many locations including Central pacific gyre, Pacific Ocean, Caribbean Sea, Kugenuma, Kanagawa, Los Angeles, USA, Northern Vietnam, Odaiba, Tokyo, Japan, Marbella Beach, Costa Rica	Hirai et. al. 2011
NPs	Hexane/DCM, CGC-ECD-MD	130 – 16000	Tokyo bay, Japan	Mato et. al., 2001
	n-Hexane, GCMS	0.7 – 3936	Many locations including Central pacific gyre, Pacific Ocean, Caribbean Sea, Kugenuma, Kanagawa, Los Angeles, USA, Northern Vietnam, Odaiba, Tokyo, Japan, Marbella Beach, Costa	Hirai et. al. 2011

OPs	n-Hexane, GCMS	0.0 – 154	Rica	Hirai et. al. 2011
			Many locations including Central pacific gyre, Pacific Ocean, Caribbean Sea, Kugenuma, Kanagawa, Los Angeles, USA, Northern Vietnam, Odaiba, Tokyo, Japan, Marbella Beach, Costa Rica	

\*. <sup>a</sup>from unidentified object comprised of PVC; <sup>b</sup> only phenanthrene studied; <sup>†</sup> concentration in µg/g; <sup>‡</sup> concentration in ng/g; Aqua Regia: HCl + HNO<sub>3</sub> in a ratio of 3:1; AFS: atomic fluorescence spectroscopy ; ICP-MS: inductively coupled plasma mass spectrophotometer; ICP-OES: inductively coupled plasma-optical emission spectrometry; FAAS: Flame Atomic Absorption Spectrometry; FP-XRF: field-portable-x-ray fluorescence; cGC-ECD-MD: capillary gas chromatograph equipped with electron capture detector and mass detector; GC-ECD: gas chromatograph equipped with electron capture detector; LSC: liquid scintillation counting; GC-ITMS: gas chromatography-ion-trap mass spectrometers; QqLIT-MS/MS: liquid chromatography system coupled to a quadrupole linear ion trap tandem mass spectrometer;

The concentrations varied among locations, indicating that the contamination represents a local problem; industrialized areas (especially areas experiencing crude oil related activities or have history of crude oil pollution) have higher concentrations than remote areas. Also, concentrations are controlled by discoloration of microplastic with yellowed (discolored) ones generally having higher concentration. However, few toxic metals and organic chemicals have generally been studied, which is very low when compared with over 300 plastic additives used with potential migration or release and potentially contaminate the environment. More study is needed to quantify more of these potentially toxic substances (PoTSs, coined by Hahladakis et. al., 2018) on microplastics. Majority of PoTSs are largely additives and have been reviewed recently by Hahladakis et. al., (2018). Also, research is needed to understand/know the sources of toxic chemicals found on microplastics, whether they came from additives or from ambient environment during particle exposure or they came from the two means working synergistically. Initial concentrations of a particular toxic chemical may be increased due to that particular chemical present in the plastic as additives. For example, very high concentration (~ 10 000 ng/g) of decabromo diphenyl ether (BDE209) on microplastics reported by Hirai et al., (2011) is most likely the result of its use as an additive rather than uptake from seawater. Another example is the concentrations of Ni and Pb in the microplastics from lake sediment and water were about equal to those in the macroplastic litters (Wang et. al., 2017) suggesting that the concentration was from additives used in the production of the plastic.

## 2.1 Heavy metals

Metals that are of high density are defined as heavy metals. Specifically, metals with density greater than 5 g/cm<sup>3</sup> and adversely affecting the ecosystem. Heavy metals are ubiquitous and find their way into the environment by natural means and through human activities (Enyoh et. al., 2018; Verla et. al, 2019b). The sources of heavy metals in the environment are varied including natural weathering and mining of the earth's crust, soil erosion, urban runoff, industrial effluents, sewage discharge, pesticides application, and many others (Morais et al., 2012; Verla et, al, 2019b). Their pollution is particularly common where there are high anthropogenic pressures such harbours and marinas. Similarly, harbours and marinas are also known to have high abundance of microplastics originated from human activities (Browne et al., 2011). They interact while in the environment, with heavy metals attaching on the surface of microplastics.

Evidence of attachment of heavy metals onto microplastics has been highlighted in recent years and reports have suggested that toxic metals are attached in high concentrations. Holmes et. al., (2012) studying adsorbed metals on polyethylene resin pellets collected from four beaches in south west England using inductively coupled plasma-mass spectrometer (ICP-MS) found mean concentrations range of metal distribution in the order; Cr (44 – 430 µg/g) > Ni (40 – 131 µg/g) > Fe (41 – 97.8 µg/g) > Co (17.7 – 107 µg/g) > Cd (1.09 – 76.7 µg/g) > Al (16.9 – 55.8 µg/g) > Zn (0.299 – 23.3 µg/g) > Mn (1.16 – 20.5 µg/g) > Cu (0.064 – 1.32 µg/g) respectively. These are high concentrations when in comparison with touchstone values for these metals in the marine environment.

Over a 12 month period, Rochman and coworkers (2014) studied metal accumulation on recently manufactured microplastics such as PET, HDPE, PVC, LDPE and PP, at three locations in San Diego Bay, USA and reported final



average concentrations for all polymers at the end of the 12 months were 4.16, 3.8 and 0.8  $\mu\text{g/g}$  for Zn, Cd and Pb respectively.

More recently, Munier and Bendell (2018) via atomic absorption spectroscopy studied different toxic metals sorped on different microplastics formed from plastic debris (two types; recently manufactured and field) in nine urban intertidal regions in Burrard Inlet, Vancouver, British Columbia, Canada. The studied microplastics include PVC, Nylon, PP, PET, PS, LDPE, HDPE, PC, PE and PUR while metals include Cd, Cu, Zn and Pb. The range of mean metal concentration reported on the different microplastic surfaces were: Cd; 0.37  $\mu\text{g/g}$  on PP to 1.77  $\mu\text{g/g}$  on LDPE, Cu; 2.93  $\mu\text{g/g}$  on Nylon to 47.53  $\mu\text{g/g}$  on LDPE, Zn; 4.3  $\mu\text{g/g}$  on PVC to 604.24  $\mu\text{g/g}$  on LDPE, Pb; 0.71  $\mu\text{g/g}$  on PET to 17.68  $\mu\text{g/g}$  on LDPE. LDPE generally had greater amounts of extracted metals. However, the greatest concentrations of 188  $\mu\text{g/g}$ , 6667  $\mu\text{g/g}$ , 698,000  $\mu\text{g/g}$  and 930  $\mu\text{g/g}$  of copper, zinc, lead and cadmium respectively was recovered from an unidentified object comprised of PVC. Data from the study suggest that the concentrations of recovered metal are similar from the two sources (recently manufactured and field) except for cadmium. These values were equally as great as that reported (Holmes et al., 2012; Rochman et al., 2014).

One study recently examined eight heavy metals in association with isolated microplastics from eight different farms in China (Mohsen et al., 2019). Six of the farms were culture pond and the remaining two farms were open areas for culturing sea cucumber. The analysis was done using inductively coupled plasma mass spectrophotometer (ICP-MS; for Cd), atomic fluorescence spectroscopy for As and other metals by inductively coupled plasma-optical emission spectrometry (ICP-OES). The reported range of the average concentrations of metals such as As, Cd, Cr, Cu, Mn, Ni, Pb and Zn in association with the MPs were as follows: 0.35–2.89 mg/kg, 0.058–0.99 mg/kg, 4.43–37.47 mg/kg, 1.37–21.67 mg/kg, 7.57–98.35 mg/kg, 1.31–43.2 mg/kg, 2.56–40.8 mg/kg, 16.44–1190 mg/kg, respectively. Data from the study suggest that heavy metal concentration associated with the MPs is not an indicator for the heavy metal concentrations in sea cucumber (Mohsen et al., 2019).

The reviewed studies have implicated high load on toxic metals on microplastics surface and confirming the potentiality of microplastics as alternative source or sink of toxic metals contaminant in the marine environment. However, data is limited regarding toxic metals adsorption onto microplastics presence in soil or air as they are air-borne (Dris et al., 2016; Gasperi et al., 2018; Allen et al., 2019; Enyoh and Verla, 2019).

## 2.2 Organic pollutant

Organic pollutants are pollutants that are organic in nature i.e basically containing carbon covalently bonded with other compounds. Some are persistent when they are in the environment regarded as persistent organic pollutants (POPs) such as PCBs and OCPs. POPs are resistant to degradation through biochemical and photolytic processes (Ritter et al., 2007) and can bioaccumulate with potential adverse impacts on the ecosystem. They are easily transported from their source and easily reconcentrated in the new environment to potential toxic levels. POPs sources could be from natural means such through volcanoes and various biosynthetic pathways or artificial means through total synthesis of chemicals (El-Shahawi et al., 2010). POPs are lipophilic in nature and have low solubility. They tend to be associated to the suspended particles in the water column due to their low solubility and accumulate on microplastics. Therefore, in tandem with microplastics the negative effects could be doubled. There are many reports in recent years concerning loads of organic pollutant adsorbed onto microplastics. Literature reveals substances that have received much attention include poly aromatic hydrocarbons (e.g flouranthene, phenanthrene etc) and persistent organic pollutants such as polychlorinated biphenyls (PCBs), the insecticide DDT and its degradation product p,p'-DDE, as well as hexachlorocyclohexane isomers (HCHs).

### 2.2.1 Polychlorinated biphenyl's (PCB's)

Polychlorinated biphenyl's (PCB's) are mixtures of up to 209 individual chlorinated compounds (known as congeners), of which 113 are known to be present in the environment (Pascal et al., 2005; NWF, 1994). The first report of PCB absorbed on PS in concentration of 5000 ng/g; presumably from sea water, was reported in 1972 (Carpenter et al., 1972b). Gregory et al. (1978), when examining the accumulation and distribution of virgin plastic granules on New Zealand beaches also reported the significant presence of PCBs sorbed to colored polyethylene pellets found in sediment in high concentrations. Concentrations have increased over time to reaching 18700 ng/g (Inger et al., 2014).

To the best of our knowledge, there was no literature concerning absorbed PCBs on microplastics from late 70's until early 2001, thereby revealing a gap in data. However, since then 8 papers have been published since 2001 till date which covers many locations suggesting increasing interest following growing interest in microplastic pollution by researchers globally.

In 2001, Mato and colleagues analyzed polypropylene resin pellets collected from four coastal sites in Japan: Kasai Seaside Park, Keihin Canal (Tokyo Bay), Kugenuma Beach (Pacific Ocean), and Shioda Beach (Sea of Japan) and identified PCBs in concentration range of 97 ng/g -117 ng/g. Variability in PCBs concentrations in beached resin pellets from Tokyo, Japan was also studied by Endo et. al. (2005). Fifty-five resin pellets individually analyzed revealed high variability in concentrations ranging from < 28 to 2,300 ng/g, which is due to pellet discoloration and regional differences.

Rios et. al., (2007), analyzed plastic samples collected from the North Pacific Ocean and coastal sites in California, Hawaii. Plastic samples were extracted with 150 ml of dichloromethane for 12 h using Soxhlet apparatus and the organic pollutant fraction analyzed by GCMS. Total PCBs concentrations reported ranged from 27–980 ng/g while the congeners most common include PCB-52, 101, 118, and 170.

Karapanagioti et. al., (2009) analyzed plastic pellets sampled from Kato Achaia, Greece. Sampled pellets were extracted with hexane and PCBs concentration measured by gas chromatograph equipped with ion-trap mass spectrometer on MS/MS mode. Results revealed PCBs concentration ranging from 3590 n/g to 10125 ng/g. Furthermore, PCB-138 was reported as the most common in comparison with other PCBs congeners (Karapanagioti et. al., 2009). Fries et al., (2010) reported PCBs concentration ranged from 0.02 ng/g to 15.56 ng/g on microplastics found on two beaches in Portugal.

Hirai and coworkers (2011) reported PCBs concentration range of 1 – 1000 ng/g from microplastic fragments sampled from open oceans, remote and urban beaches. Plastic resin pellets collected from remote islands in the Pacific, Atlantic, and Indian Oceans and the Caribbean Sea were analyzed for PCBs by Heskett et. al. (2012). The report revealed total PCBs concentrations range of 0.1-9.9 ng/g.

Long term decrease (1989-2008) in total PCBs concentrations on yellow polyethylene pellets from three South African coastal waters (West Coast Park, Port Elizabeth and Woody Cape) was reported by Ryan et. al., (2012). The concentrations dropped was from 113 ng/g (1989) to 61 ng/g (2008) in West Coast Park; 41 ng/g (1989) to 27 ng/g (2008) in Port Elizabeth and 56 ng/g (1989) to 25 ng/g (2008) in Woody Cape respectively. The reduction may be a function of plastic age (Mato et. al., 2001; Rios et. al., 2007). With the view of establishing background concentrations for International Pellet Watch, Heskett and coworkers in 2012 measured POPs in plastic resin pellets from remote islands in Spain (Canary Islands), British territory (Saint Helena), Australia (Territory of the Cocos (Keeling) Islands), US (Island of Hawaii and Island of Oahu) and Barbados (Island of Oahu) and revealed median concentrations of total-13 PCBs in pellet samples from the remote islands ranged from 0.1 to 9.9 ng/g-pellet. Concentration that was 1-3 order less than those in pellets from industrialized coastal zones as reported by Ogata et al., (2009), suggesting that plastic pellets from industrialized zone accumulate higher concentration of PCBs. The chemical structures of common congeners of PCBs reported in literature are presented in figure 2.

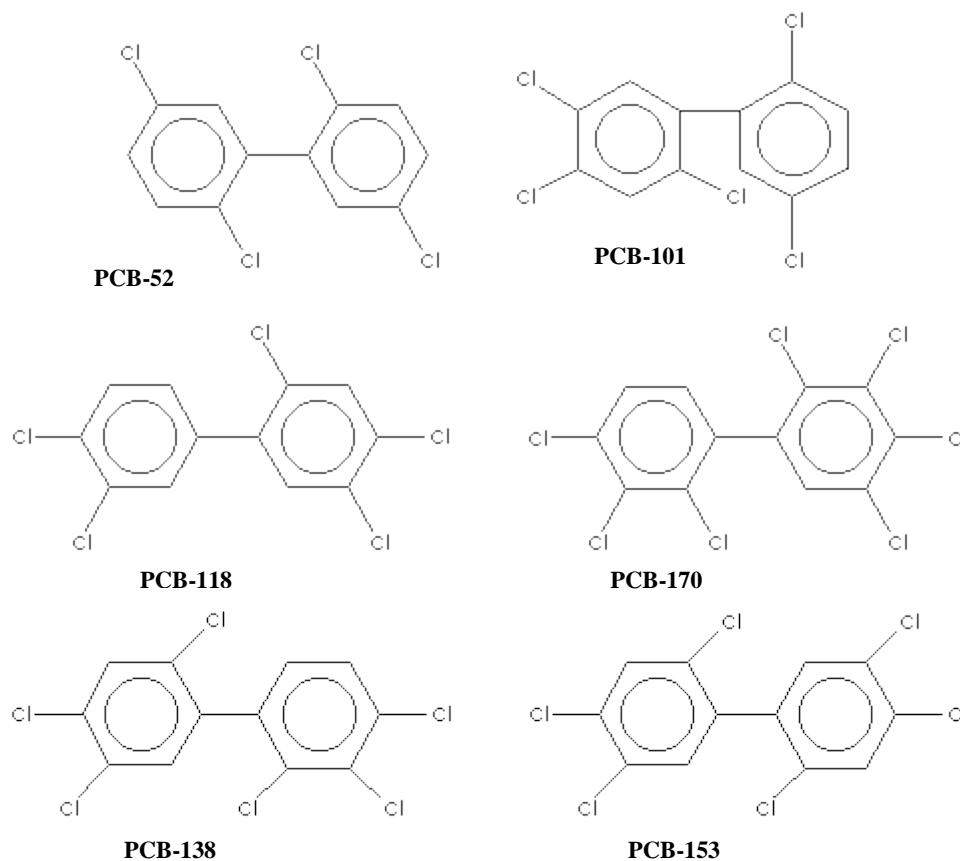


Figure 2: Chemical structures of common PCB congeners found on microplastic surface from beaches

### 2.2.2 Poly aromatic hydrocarbon (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) sometimes called polynuclear aromatic hydrocarbons are composed of multiple aromatic rings (organic rings in which the electrons are delocalized) with simplest form of two rings (naphthalene) and three rings (anthracene and/or phenanthrene). Studies have reported their presence on microplastics at varying concentrations of which; fluoranthene (Fluo), phenanthrene (Phe), anthracene (Anth), 3-methylphenanthrene (3-MP), 9-methylphenanthrene (9-MP), 2-methylphenanthrene (2-MP), 1-methylphenanthrene (1-MP), pyrene (Py), benzo[b]fluorene (a-MPy), 2-methylpyrene (c-MPy), 1-methylpyrene (d-MPy), benzo[b]fluoranthene (BbF), chrysene (Chry), 5 methylated isomers of chrysene or benz[a]anthracene, 4-methylpyrene (b-MPy), benzo[j]fluoranthene (BjF), benz[a]anthracene (BaA), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (Pery), indeno[1,2,3-cd]pyrene (IndPy), benzo[ghi]perylene (BghiP), 4H-cyclopenta[def]phenanthrene (CPP) and coronene (Cor) have generally been quantified (Rios et. al., 2007; Karapanagioti et. al., 2009; Saha et al. 2009; Yeo et. al., 2017).

In a study conducted by Rios et. al., (2007) on microplastics sampled from North Pacific Gyre, and selected sites in California, Hawaii, and from Guadalupe Island, Mexico reported adsorbed PAHs concentrations in the range of 39 to 1200 ng/g. In the same study, analysis of discolored (yellowed) plastic revealed higher concentration range of 6100 to 12,000 ng/g (Rios et. al., 2007). The fragment samples taken from the bank of the San Gabriel River, at the beach, and on the sea surface also presented high concentrations (6200–9200 ng/g) of PAHs (Rios et. al., 2007). The literature data pointed out that discolored microplastics accumulate higher concentration of PAHs than newer microplastics.

Teuten et al. (2007) observed PAH (phenanthrene) at concentrations  $10^6$  higher on polystyrene pellets than in surrounding water. Concentration of total-PAHs in pellets (ng/g-pellet) sampled from Kato Achaia, Greece ranged from 66 ng/g to 637 ng/g (Karapanagioti et. al., 2009). However, lower PAH concentration ranging from 0.2 to

319.2 ng/g was reported from microplastics found on two Portuguese beaches (Fries et al., 2010). Also, Hirai et al., (2011) analyzed plastic fragments (<10 mm) collected from pelagic and neritic stations, revealed a range of 1–10,000 ng/g for PAHs. The variability in the concentration and composition of PAHs at different sediment depths in a sandy beach located in Santos Bay on the southeastern coast of São Paulo state, Brazil was studied (Fisner et al., 2013). In the study, some variability with depth with highest concentration of PAHs in pellets collected in the surface layer of the sediment (0–10 cm with 1996 ng/g), with smaller peaks recorded at 60–70 cm and 30–40 cm (1336 ng/g and 1004 ng/g, respectively). The concentration of total-priority PAHs ranged between 198 and 1042 ng/g while total-PAHs ranged from 637 ng/g to 1996 ng/g. Generally, in comparison with potential toxicity level set by NOAA showed the concentration was low (Fisner et al., 2013).

Mizukawa et al. (2013) reported, PAH concentration variations of up to 2 orders of magnitude between individual countries within a region. More recently, Yeo et al., (2017) following IPW monitoring study reported that Europe at Sao Torpes Beach, Sines in Portugal (24400 ng/g-pellet) and Forth Estuary in UK (164900 ng/g-pellet) were highest in concentrations of total PAHs on plastic pellets collected from 75 locations in 26 countries. The authors attributed these high concentrations to crude oil pollution. Generally, based on the categorization for International Pellet Watch, the recorded PAHs levels were moderate to extreme for Western Europe (especially around the North Sea) while moderate to high concentrations was reported for East Asia (Japan and China) and North America respectively. However, South East Asia, Oceania, South America, and Africa (except for site with history of oil spillage or experiences petroleum-related activities) recorded low concentrations. For example, plastic pellets collected from Chemu Lagoon Beach located close to Tema oil refinery in Ghana, was highly polluted with 2751 ng/g-pellet (Yeo et al., 2017), thus confirming the influence of crude oil pollution in increasing levels of PAHs loaded on the surface of microplastics.

### **2.2.3 Organochlorine Pesticides (OCPs)**

Organochlorine (OC) pesticides are synthetic pesticides which belong to the group of chlorinated hydrocarbon derivatives, widely used in chemical industry and in agriculture. Reported OCPs in literature include; Dichlorodiphenyltrichloroethane and related compounds (DDTs), Hexachlorocyclohexane (HCH) isomers, Chlordanes, Cyclodienes, Mirex, Hopanes: natural substances, Hexachlorobenzene.

#### ***Dichlorodiphenyltrichloroethane and related compounds (DDTs)***

Dichlorodiphenyldichloroethylene (DDE) concentrations on microplastics (specifically, PP) collected from four coastal sites in Japan was reported to range from 0.16 ng/g to 3.1 ng/g (Mato et al., 2001). Ogata et al. (2009) reported the occurrence of DDTs (DDT, DDD and DDE) in plastic pellets collected at 30 beaches from 17 countries and 5 continents (North America, Europe, Asia, Africa and Oceania). The highest concentrations of total-DDTs from the International Pellets Watch (IPW), implicated Hermosa Beach, California, USA (267 ng/g) while Bay of Maputo, Mozambique and South Durban, South Africa had concentrations of 4.49 ng/g and 2.43 ng/g respectively (Ogata et al., 2009). Dichloro-Diphenyl-Trichloroethane (DDT) and dichlorodiphenyldichloroethane (DDD) concentrations were measured by GC equipped with electron capture detector (GC-ECD) while DDE concentrations was measured by gas chromatograph equipped with ion-trap mass spectrometer on MS/MS mode from plastic pellets sampled from Kato Achaia beach, Greece (Karapanagioti et al., 2009). The reported concentrations ranged from 0.8 ng/g to 1.9 ng/g for DDT, 0.2 ng/g to 2.6 ng/g for DDD and 2.7 ng/g to 88 ng/g for DDE respectively. A study by Colabuono et al., (2010) on OCPs on microplastics ingested by seabird revealed total-DDT concentration range of 64.4–87.7 ng/g. Also, among the 25 different and related OCPs studied, p,p-DDE had the highest concentrations ranging from 68.0 to 99.0 ng/g. The concentrations of DDT and related compounds generally vary by location and methodology. Another conclusion is that concentrations found on microplastics ingested by seabirds were higher than in sediment. In 2012, DDTs concentrations (sum of p,p-DDT, p,p-DDD, and p,p-DDE) was reported to ranged from 0.7 to 4.1 ng/g-pellet from plastic pellets sampled from remote islands in six locations (Heskett et al., 2012). The study further implicated DDT (70 – 91 % of total) as the most distributed over the degradation products viz DDD and DDE.

#### ***Hexachlorocyclohexane (HCH) isomers***

Hexachlorocyclohexanes (HCHs) concentrations measured by GC equipped with electron capture detector (GC-ECD) from Plastic pellets sampled from Kato Achaia beach, Greece revealed total-HCH in the range of 1.02 ng/g to 1.65 ng/g (Karapanagioti et al., 2009). Also in the study, the different HCH-isomers studied showed concentrations

ranging from 0.2 ng/g to 0.31 ng/g for  $\alpha$ HCH, from 0.48 ng/g to 0.53 ng/g for  $\beta$ HCH, from 0.15 ng/g to 0.32 ng/g for  $\gamma$ HCH and from 0.06 ng/g to 0.25 ng/g for  $\sigma$ HCH (Karapanagioti et al., 2009). These concentrations were generally low and close to procedural blank used in the study, suggesting low HCH in Kato Achaia beach, Greece. A study reported in 2012 on plastic pellets collected from remote islands around Europe and America pelagic zones found HCH concentrations in the range of 0.2–19.3 ng/g-pellet (Heskett et al., 2012). HCH isomers had concentration range of 0.0-0.7 ng/g ( $\alpha$ HCH), nd-0.7 ( $\beta$ HCH), nd-15.8 ( $\gamma$ HCH) and nd-1.6 ( $\sigma$ HCH) respectively. Although, the concentrations were low generally, larger concentrations were recorded at St. Helena Island attributed to lindane use on island during the study period (Heskett et al., 2012), thus suggesting that concentrations are influenced by local activities.

### ***Chlordane, Cyclodienes, Mirex, Hexachlorobenzene and Hopanes***

Reported levels of chlordane, cyclodienes, mirex and hexachlorobenzene adhered to microplastics in the natural environment is lacking due to lack of data. However, there are reports of their adsorption on microplastics collected from seabird. Calabuono et al., (2012), using gas chromatograph with an electron capture detector (GC-ECD) assessed microplastics found in the digestive tract of eight species of *Procellariiformes* collected in southern Brazil and reported total chlordane levels ranging from 4.29-14.4 ng/g, total cyclodienes levels ranged from 2.41 to 50.9 ng/g, total mirex levels ranged from 6.48 to 14.6 ng/g and total hexachlorobenzene ranged from 12.4 to 17.5 ng/g respectively. The authors pointed that the levels were similar to levels in the tissues of majority of seabirds around the world. The authors recommended that studies on the contamination of these pollutants in seabirds with high frequencies of plastic ingestion and the development of research that links such information are essential to understanding whether (and how) the transfer of organic pollutants from plastics to marine organisms should be conducted (Calabuono et al., 2012).

High concentrations of total hopanes (8300 ng/g to 62000 ng/g) were recorded in a monitoring study on microplastics sampled from eight locations on the coast of Portugal (Mizukawa et al., 2013). Data from the study revealed that, among the congeners, homohopanes (ranging from C<sub>31</sub> to C<sub>35</sub>) were relatively abundant. More recently, following IPW from Western Europe, East Asia, Oceania, South America and Africa; Yeo et al., (2017) reported total hopanes level in plastic resin pellet ranged from 1700 ng/g to 101000 ng/g which showed no spatial pattern. However, hopanes concentrations sorped on microplastics are influenced by crude oil-related pollution. Reports have indicated higher concentrations of hopanes in the Northern Hemisphere (China, Japan, UK, France, Germany, Portugal, and Spain), particularly around the North Sea due to these regions having a long history of oil development and oil tanker routes (Yeo et al., 2017). Zakaria et al. (2000;2001) pointed that crude oil origin affects the composition of hopanes, and can be used for source identification of oil pollution.

#### ***2.2.4 Other organic pollutants***

##### ***Polybrominated diphenyl ethers (PBDEs)***

PBDEs rarely degrade when in the environment. Although their carcinogenic effect is not yet established, EPA assigns the cancer category Group D (not classifiable as to human carcinogenicity) to mono-, di-, tri-, tetra-, penta-, hexa-, octa-, and nonaBDEs and no classification for specific congeners 2,2',4,4'-tetraBDE, 2,2',4,4',5-pentaBDE, and 2,2',4,4',5,5'-hexaBDE due to inadequate information on their cancer risk (Breysse, 2017). Just like many other hydrophobic contaminant, PBDEs have been reported to adhere on plastic fragment from marine environment. The distribution of PBDEs levels on microplastics are spatially based (or regional differences), plastic type and dependent on local anthropogenic activities. For example, in terms of microplastic type, very high concentration (9909 ng/g) was reported on PP collected from central pacific gyre while from the same study area, total-PDBEs level on PE was very low (0.3 ng/g) (Hirai et al., 2011). Generally in the study the levels ranged from 0.3 ng/g to 9909 ng/g with remote areas having lower concentration compared to open seas where people frequent and under high anthropogenic pressure. PBDEs are airborne pollutant and can be transported from the continents to both coastal and open sea through aerosol (Gambaro et al., 2009) and dust. Microplastics are airborne pollutant (Dris et al., 2016; Gasperi et al., 2018; Allen et al., 2019) and they may transport PBDEs with them. Therefore, studies are required to quantify PBDEs levels on atmospheric microplastics in many locations of the world to inform on ecological as well as human risk associated with PBDEs adhered on airborne microplastics.

BDE-209 is one common PBDEs congener normally occurring in very high concentrations, although also depended on quantity of BDE-209 additives, anthropogenic activities and vary by location. Hirai et al., (2011) reported 100 %

of total-PBDE was BDE-209 in an open ocean while a 1 % for location in remote area. Generally, the level of total-PDBEs correlated strongly with BDE-209 level; high BDE-209 concentrations will cause high total-PDBEs concentrations on microplastic.

### ***Perfluorinated compounds (PFCs)***

PFCs also called perfluorinated alkyl substances (PFASs) are a large group of chemicals used in industrial and commercial applications due to their inertia and resistance to physical, chemical and biological degradation (Llorca et al., 2012). They have been related to different toxicological effects (e.g., disruption of the thyroid hormones and the metabolism of high-density lipoproteins, cholesterol and triglycerides (Lau et al., 2007; Peden-Adams et al., 2008). Data on adsorbed PFCs concentrations on microplastics is limited. However, one study determined levels and fate of perfluoroalkyl substances in beached plastic pellets collected from Corfu Island, Lavrio beach, Kato Achaia beach, Leros Island and Loutropyrgos beach in Greece and reported concentration range of 10 to 180 ng/Kg (Llorca et al., 2014). A further study by Llorca and coworkers on the capacity of three microplastics, that include HDPE, PS and polystyrene carboxylate (PS-COOH), to sorb 18 perfluoroalkyl substances (PFASs; including carboxylic acids, sulphonates and one sulphonamide) from the surrounding waters (freshwater and seawater) revealed the order of PS > PS-COOH > HDPE for their adsorption of PFASs (Llorca et al., 2018). There is need for more study to quantify concentrations of adsorbed PFASs on microplastics from more locations, in order to understand better their distribution in the environment.

### ***Bisphenol A (BPA)***

BPA is a constituent monomer in polycarbonate which is widely used in food and beverage containers. The compound is persistent, but their instability within plastic products facilitates leaching and their high prevalence in aquatic environments has been widely reported, particularly in landfill leachates (vom Saal and Myers, 2008). Studies are lacking regarding the level of bisphenol A adhered on microplastic surface. One study reported concentrations range of <1 to 729.9 ng/g for microplastic sampled from remote, open ocean and urban beaches from America and Europe (Hirai et al., 2011).

### ***Aliphatic hydrocarbons***

Aliphatic hydrocarbons have not been reported to negatively affect organisms in the environment, perhaps due to their easy degradation when compared to other toxic pollutants such as PAHs, PCBs and OCPs (Webster et al., 2003). However, those of higher carbon groups (C<sub>28</sub>-C<sub>40</sub>), particularly some n-alkanes are difficult to be degraded biologically (Brakstad and Bonaunet, 2006; Okoh, 2006). Aside this, Rios et al., (2007) stated that they can help in differentiating organic matter sources in the environment whether biogenic or petrogenic. Evidence of their concentrations on microplastics is very limited. One study reported a total aliphatic concentration (C<sub>12</sub>-C<sub>36</sub>) range of 1.1 – 8600 ng/g from sampled plastic pellets from the North Pacific Ocean, and coastal sites in California, Hawaii and regurgitated stomach contents from a Laysan albatross colony on Guadalupe Island, Mexico. Also from the study, the industrial sites had highest levels of n-alkanes compared to other study locations. This finding suggest that industrial activities may increase levels of aliphatic hydrocarbons adhered onto microplastics.

### ***Octylphenols (OPs) and Nonylphenols (NPs)***

Derivatives of OPs and NPs are used as additives for plastics and some other products like laundry and dish soap, detergent, paint etc. Many products that contain OPs and NPs have "down-the-drain" applications, therefore, making them easily introduced into the water supply, river water, sediments, soil and groundwater (Thiele et al., 1997). Another source of their presence in the environment involves the breakdown of ethoxylates (Octylphenol ethoxylates; OPEs and nonylphenol ethoxylates; NPEs) as well as leaching from plastic debris (Staniszewska et al., 2015). OPs and NPs persist in the environment and are particularly toxic with their endocrine disrupting activities (Gabriel et al., 2008; Soares et al., 2008; Lu et al., 2014).

Evidence of the presence on microplastics is limited especially for OPs. Information concerning the concentrations of OPs on microplastics was only reported in a study by Hirai et al., (2011). OPs presence has been reported in leachates (0.1-154 ng/g) from waste disposal sites (containing considerable amounts of plastics) across Asia (reviewed by Teuten et al., 2009). The review studies didn't attempt to confirm their sources whether it is from degrading plastics present at the waste disposal site, which may be achieved using the principal components

analysis. On the other hand, the concentration of nonylphenols was studied on plastic pellets collected in 1997 and 1998 from four beaches in Tokyo bay (Mato et. al., 2001). In their report the levels ranged from 130 ng/g to 16000 ng/g, concentration that was 2 orders higher than sediment from the same location. The concentrations of NPs in the environment have been reported to be reducing over the years. Studies reported in 2007 and 2011 found lower concentrations of NPs, concentrations which ranged from 0.7 to 3936 ng/g (Teuten et. al. 2007; Hirai et. al., 2011). We found no recent study published on OPs and NPs levels adhered on microplastics. This exposes scarcity of data concerning their distribution in the environment by microplastics. This can be a call for concern as consumption of these chemicals can be hazardous for both terrestrial and aquatic animals.

### 3. Adsorption and desorption mechanism of toxic chemicals onto microplastics

Microplastics serve as carrier for toxic chemicals such as heavy metals and organic pollutants in the environment. This is possible by pollutants adsorbing onto microplastics surface. The adsorption of toxic chemicals on microplastics surface is due to the large surface area of microplastics (as high as 4.37 m<sup>2</sup>/g; measured using the Brunauer-Emmett-Teller (BET) method reported by Teuten et. al., 2007). Furthermore, induced electrostatic charge on the highly resistive plastic caused by high-speed manufacturing equipment during plastic production can increase the pickup of pollutants while in the environment. Some studies in 1950s have demonstrated the effect of static charge on plastic surface to pickup of atmospheric dust (Woodland and Ziegler, 1951; Skimmer et al., 1956). Electrostatic charge as high as -9 kv was measured on moving plastic, which make them more susceptible to contamination by airborne pollutants (Lester et al., 1966). Data from the study by Lester et. al., (1966) showed that pollutant can adhere to the plastic surface under many environmental conditions.

The adsorption and desorption mechanisms of toxic chemicals to plastics are varied and complex and remain relatively unexplored by researchers. The lack of exploration, hence lack of the information is partly due to lack standard analytical procedure or operation protocols (SOP) (Verla et. al., 2019a). However, the plausible mechanism of sorption and desorption of toxic chemicals onto or from microplastics surface are discussed in this section.

The sorption/desorption mechanism can be monitored or studied using some spectroscopic techniques (reviewed by Verla et al., 2019a) as well as using different sorption kinetics and isotherms models such as pseudo-first-order (PFO), pseudo-second-order (PSO), or the intra-particle models (Wu et al., 2016; Hu et al., 2017; Wang and Wang, 2018a; 2018b), linear, Freundlich, Langmuir models, Polanyi-Dubinin-Manes model (Hüffer and Hofmann, 2016; Sven et. al., 2019), pore-volume diffusion model (PVDM), pore-volume and surface diffusion model (PVSDM) (Ocampo-Perez et al., 2010; Souza et al., 2017; Ocampo-Perez et al., 2017), poly-parameter linear free energy relationship (Hüffer et al. 2018; Sven et. al., 2019) and film-pore mass transfer (FPMT) (Guo and Wang, 2019).

The use of these models is dependent on the laboratory experimental framework. Some of the models have significant limitations e.g PFO and PSO models, which only considers adsorption step on the active sites and predicts the internal diffusion while ignoring the external diffusion. In the use of linear, freundlich, langmuir isotherms models, assumption is made that there is a local equilibrium between the contaminated aqueous medium and microplastics, an assumption that may be misleading (Sven et. al., 2019). More refined models such as poly-parameter linear free energy relationship and novel FPMT recently developed, was reported to be the best so far (Sven et. al., 2019; Guo and Wang, 2019). In their study, using the novel FPMT model, phenomenological Sr<sup>2+</sup> sorption onto spheroids primary microplastics was achieved (Guo and Wang, 2019).

#### 3.1 Adsorption mechanism

Microplastics consist of various types of polymers (e.g., polypropylene, polyethylene, polystyrene etc.) having different surface structures and, therefore, different affinities to pollutants. The adsorption generally involves the incorporation of toxic chemicals into the pitted surface microplastics while the adsorption capacities are influenced by weathering processes (Holmes et al., 2014) and plastic type. Plastic types play an important role on the type of toxic chemicals sorped from the environment. For example, an *in situ* adsorption experiment demonstrated greater sorption of PCBs to PE pellets than PP pellets (Mato et al., 2002), laboratory adsorption experiments showed higher distribution coefficients of PAHs for PE than for PP (Karapanagioti and Klontza, 2007, 2008; Teuten et al., 2007; Karapanagioti et al., 2010), two alkylbenzenes sorbed more strongly to PVC than to PE (Wu et. al., 2001) and for heavy metals showed higher distribution coefficients of Zn for PS than for PVC while vice versa for Cu (Brennecke et. al., 2016). Also, the understanding of the mass transfer kinetics in the adsorption process is important to evaluate and predict the adsorption behaviors of microplastics. The sorption kinetics includes three mass transfer steps: (a)

the diffusion of sorbate across the liquid film around the sorbent (b) the diffusion of sorbate inside the sorbent, and (c) the adsorption on active sites (Guo and Wang, 2019). However, there are three plausible mechanisms by which chemicals are adhered onto microplastic particles include (1) adsorption with microplastics as hydrophobic adsorbents (2) biofilm growth assisted and (3) plastic additives and related chemicals contained with resins.

### 3.1.1 Hydrophobic adsorption of chemicals

Microplastics tend to be more hydrophobic because they exhibit low polarity on their surface. This enables the hydrophobic (water hating; immiscible in water) adsorption of chemicals onto their surfaces from seawater. They act like hydrophobic adsorbents in the environment (e.g. Sea). Microplastics are less dense than water and thus accumulate most in surface microlayer (SML) of sea water. Lipid-loving chemicals like POPs (including polychlorinated biphenyls PCBs, polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (such as DDT, DDE) have the right characteristics to adsorb and concentrate on the plastics hydrophobic surface forming a micelle shape-like structure. The extent of adsorption can be determined using the adsorption partition coefficients calculated as the ratio of pollutant concentration adhered onto microplastics before and after adsorption. A simple schematic of the adsorption mechanism process using PAH (phenanthrene) is presented in figure 3.

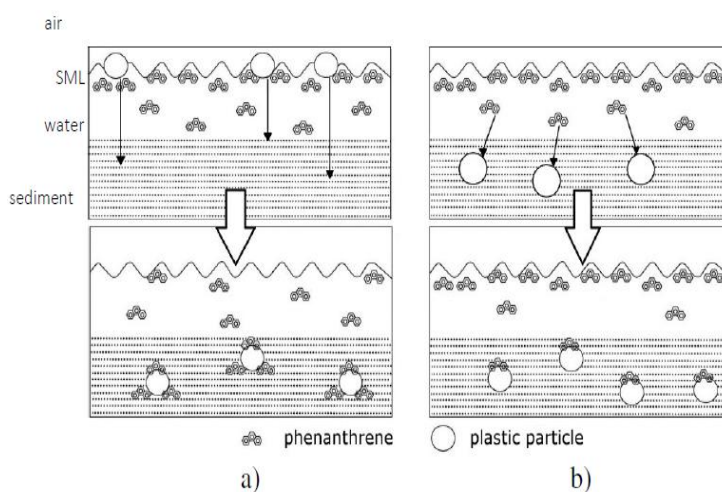


Figure 3: The mechanisms of transfer of contaminants when: a) clean microplastics are presented in SML, b) clean microplastics are presented in sediment.

Microplastics as stated earlier have low polarity on its surface. The low polarity exhibited by microplastics could also be responsible for aqueous metal ions adsorption on their surfaces. Aqueous metal ions are positively charged ( $M^+$ ) and bind by electrostatic attraction to the negatively charged groups on the surface of the plastic and neutralize their charge, forming also micelle shape-like structures (shown in Figure 4) similar to the ones presented in Figure 3a. Irrespective of adsorption medium (whether it is soil, sediment, water or air) the mechanism of adsorption is thought to follow the same principle, although the binding form might vary with different plastic types and metal ion type (cationic or anionic). Detailed studies are however required to unravel how aqueous anionic metal ions such as arsenic (As), selenium (Se), chromium VI [Cr(VI)], molybdenum (Mo) and boron (B), bind on the surface of plastics.



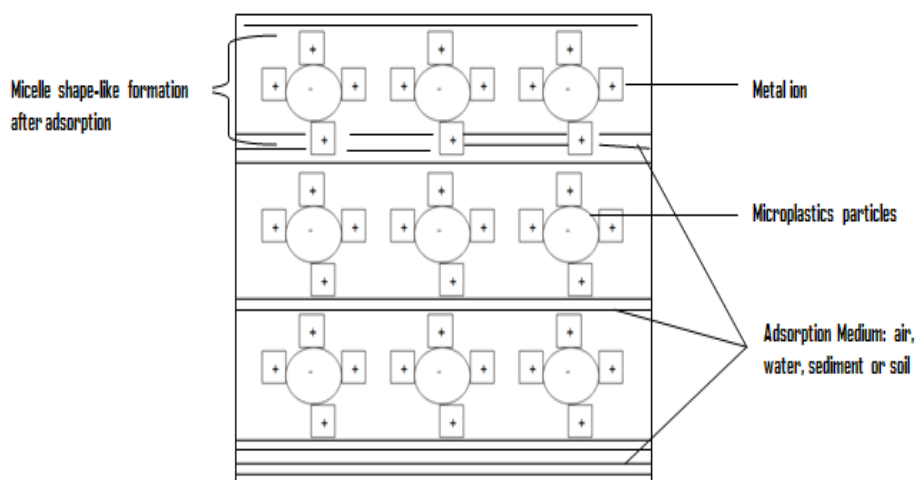


Figure 4: Schematic of adsorption of metal ion onto microplastic

The accumulation of toxic chemicals on microplastics in the environment increased with longer time. In a laboratory experiment, a rapid absorption of trace metals such as Pb, Co, Ni, Cd, Cu and Cr onto virgin polyethylene pellets suspended in trace metal-amended seawater adsorb trace metals in a Langmuir or Freundlich fashion with equilibrium partition coefficients of up to about 50 ml/g (Holmes et. al., 2012). However, the process takes longer time in the natural environment than in a controlled laboratory experiment (Fischer et al., 2007). The reason is that while plastics continue to degrade, oxygen groups are generated increasing the polarity and also the surface area are changed, which increases the porosity and charge, making the plastics surface more reactive (Mato et al., 2001; Fotopoulou et. al., 2012; Artham et. al., 2009; Holmes et al., 2012).

### 3.1.2 Biofilm growth assisted

A review study on metal immobilisation by biofilms conducted by van Hullebusch et al. (2003) revealed that biofilm is a sorbent for metals. Biofilm are formed by micro-organism through a process called quorum sensing (QS). QS is known to control gene expression in which microbial cells form matrix of extracellular polymeric substance (EPS) by adhering to each other on a living or non-living surfaces (Schauder and Bassler, 2001; Rutherford and Bassler, 2012). Biofilm are ubiquitous in nature and commonly occur on hard surfaces submerged in or exposed to an aqueous solution (Srey et. al., 2013; Solano et. al., 2014) such as microplastics accumulating in SML of sea water. The EPS may act like a ligand and by chelation may bind metals to control their mobility, distribution in the aqueous environment or directly use them within the cell (Richard, 2016).

The biofilm formation processes begin within seconds of first contact of virgin microplastic particles and ambient water (Loeb and Neihof, 1975; Christoph et al., 2017). A graphical illustration of biofilm formation process on microplastic surface is presented in Figure 5a while in Figure 5b, a biofilm attached to the surface of microplastic (in the micrograph; the plastic is HDPE) incubated in waste water for 6 month studied using scanning electron microscopy (SEM) is presented. The formation process can be monitored under SEM, however under different environmental conditions/factors as well as plastic type, different micrograph will be generated. Raymont (1980a; 1980b) pointed that biofilm growth is largely depended on light and temperature, as well as on the trophic state of the media. Characterizing chemical composition of biofilm can be achieved by Fourier-transform infrared (FT-IR) spectroscopy (Ojeda et. al., 2009), SEM-EDS (Verla et. al., 2019a), microfluidics (Rusconi et. al., 2014; Foulon et. al., 2016) and XRD (Roh et. al., 2006) may also be used. This in turn may provide insights into microbial-microplastic-toxic chemical interactions under different conditions; since community composition influences metal sorption (Muhamed and Saly, 2011; Savoca et. al., 2016).

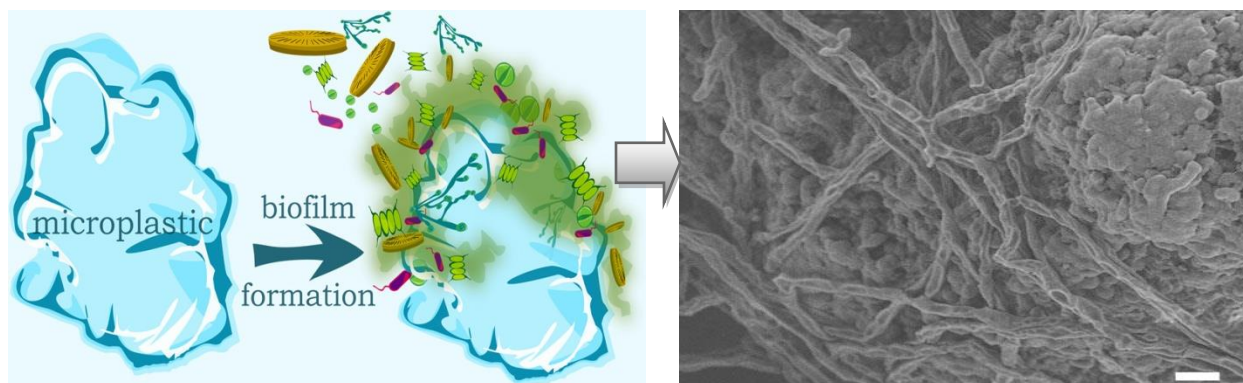


Figure 5a. Biofilm formation on the surface of microplastic (Christoph et al., 2017)

Figure 5b. Scanning electron micrograph showing a biofilm attached to a microplastic (Harrison et al., 2015).

Biofilm can increase the immiscibility (lesser polarity; high hydrophobicity) of plastic surface in water and through pitting of microbial cell, which also increase the surface area (Lobelle and Cunliffe, 2011; Zettler et al., 2014; Reisser et al., 2014). This in turn increases sorption sites on plastic surface for metals adsorption (Richard, 2016). However, from a study by Elasri and Miller (1999) on the response of a biofilm bacterial community to UV radiation suggest that formed biofilm on plastic surface may block UV light and therefore slowing down the plastic degradation processes, thus reducing the surface area and sorption sites of plastics. Hence, studies will be required to understand better the relationship between growth of biofilm and plastic degradation as conveyor of metal accumulation in the environment. Furthermore, following the high estimate (1,000-15,000 metric tons) of microbial biomass reported to be associated with global plastic debris presented in a study by Mincer and his colleagues in 2016, it became more obvious that biofilm may be playing a crucial role in toxic chemical transports by microplastics, therefore studies on microplastics serving as a vector for toxic chemicals in aquatic habitats should include biofilm as variable (Richard, 2016). This is of ecotoxicological concern as literature data pointed out that biofilm is the reason some animals are attracted to plastic as a source of food (Savoca et al., 2016) and thus potentially contaminating the base of the food chain.

Limited studies to have examined the effect of biofilm growth on adsorption of toxic chemicals on microplastics surface are based on observation through microscopic techniques rather than mechanistically driven (Reisser et al., 2014; Eich et al., 2015; Maso et al., 2016). One study conducted on San Francisco bay found that metal such as nickel (Ni), aluminum (Al) and zinc (Zn) accumulation on plastic (low-density polyethylene; LDPE and polylactic acid; PLA) is attributed to biofilm growth. Furthermore in the study data suggests that difference in plastic shape, the medium can result in variation in growth patterns of biofilm and biofouling communities (Richard, 2016). Other studies have shown that community composition influences metal sorption (Savoca et al., 2016) and sorption properties of biofilm can depend on season and biofilm maturity.

Finally, metal composition within a biofilm can increase sorption by organic pollutants. Ions within a biofilm are reported to be more labile than ions bound to ion exchange polymers, and can be used as nutrients by cells within biofilms. Again, these processes must be explored further before accurate estimates can be made regarding the potential for plastic to accumulate, transport and release heavy metals. Majority of kinetic studies on the influence of biofilm have ignored the attachment of chemicals such as HOCs (Lee et al., 2014; Wu et al., 2016).

### 3.1.3 Plastic additive and chemicals in resins

Another plausible mechanism may be from additives used in plastic production and related chemicals contained with resins. This mechanism is often common with thermosetting plastics in which the term "resin" is loosely applied. Plastic contain many synthetic chemicals as additives. These additives may vary with different polymer type. In 2000, different plastic additives reported was > 300 (Cadogan and Howick, 2010), while the groups of plastic additives with examples of hazardous chemicals has been reviewed previously (Hahladakis et al., 2018). However, most common additive is the formaldehyde, bisphenol A (BPA) and phthalates. These chemicals are added to

plastics to make it hard, durable, flexible and long-lasting. Unfortunately, they are transported with microplastics in the environment and are potentially harmful to wildlife and humans. The International Agency for Research on Cancer (IARC) classified formaldehyde as carcinogen category 1B while BPA may disrupt hormone and reproductive systems, including abnormal penis development in men (Erik, 2018). The molecular size is a key property of the additive when evaluating how fast it migrates through and out of the plastic. The smaller the additives, the faster they will migrate.

### 3.2 Desorption mechanism

The desorption reactions of toxic chemicals from microplastics in the environments, control their concentrations in solution and affect their bioavailability, leaching and toxicity. Desorption processes of pollutants from microplastic is simply referred to the process in which the pollutant maneuver from the initial position in the polymeric system to the polymer outer surface and then to the release medium viz soil, sediment, water or animal/human body. The processes may vary by the redox state of the adhered metals, desorption capacities and the binding energies of their adsorption sites. These reactions may be affected by many factors, such as pH, type of plastics, salinity, presence and concentration of organic and inorganic ligands in the release medium. If the release medium is soil or sediment, the components responsible for trace element sorption include, soil humic substances, carbonates and inorganic components (variable charge minerals and phyllosilicates) (Violante and Pigna, 2008). A detailed summary of these driving factors is shown in Figure 6

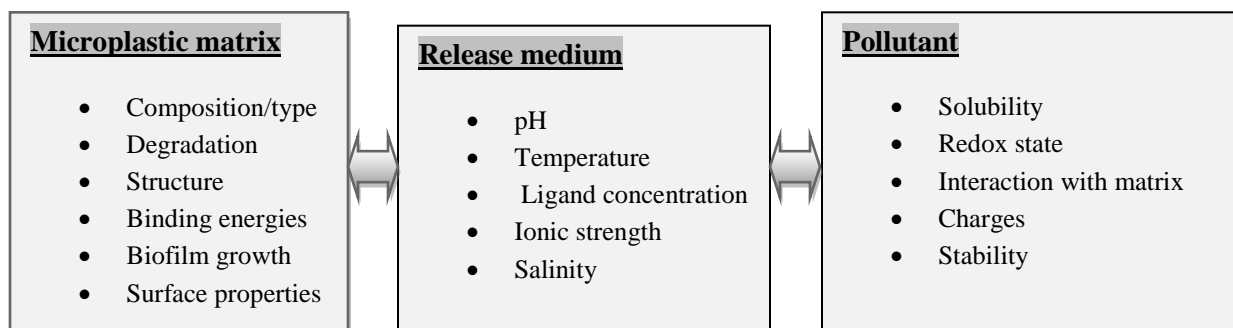


Figure 6: Summary of factors that may influence pollutant release kinetics

Desorption or release mechanisms of toxic chemicals are unclear and remain relatively unexplored by researchers. Release of pollutant from a microplastic particle to another medium is usually subdivided into two mass transfer processes viz internal mass transfer (IMT); which involves internal diffusion within the microplastic particle and external mass transfer (EMT); which involves transfer from the microplastics to the plastic particle surface in the release medium (often aqueous) (Pignatello and Xing 1996; Tcacuic et al. 2015).

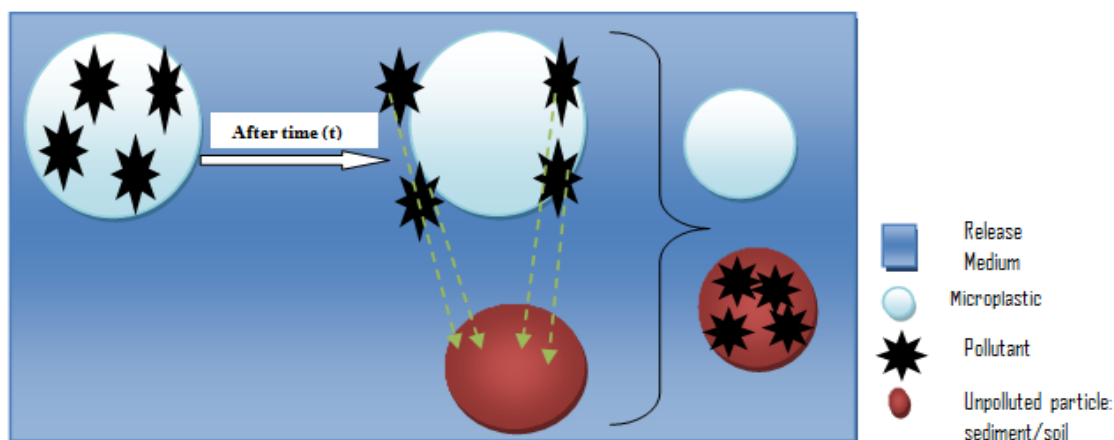


Figure 7: Graphical illustration of possible desorption/release mechanism of pollutants from microplastic surface onto clean/unpolluted particle. The adsorbed pollutant (black star) on the basis of concentration gradient, release

distance and biofilm growth will migrate and adsorb onto the clean sediment (purple ball) rich in organic material (ligands). In sediment/soil such ligands include humic and fulvic acids, root exudates and nutrients.

When an adsorbed pollutants have been transported to a new environment and come in contact with a new material e.g non-polluted sediment or soil, there may be desorption of pollutant from the microplastics onto organic or inorganic ligands present in the sediment and soil matrix (Figure 7). Teuten et al., (2007), reported desorption of PAH (e.g phenanthrene as an example used in the study) from microplastic surface to organic matter in sediment on the basis of concentration gradient. Another basis for increasing desorption in aqueous medium is the salinity level of the medium. One study recently found that there was a clear trend of decreasing sorption of DDT with increasing salinity of the aqueous medium (Bakir et. al., 2015). Generally, as pointed out by Borrirukwisitsak et al., (2012), that organic compounds becomes less soluble as salinity level rise and partitioning of organic chemicals into other phases are affected by the salt content in aqueous phase. However, desorption of phenanthrene was not affected by salinity (Bakir et. al., 2015). More study will be needed to understand how salinity affects desorption of organic pollutants from microplastics.

Assuming a mass balance in a batch study, desorption of toxic chemicals from virgin plastics pellets, may be studied using the pseudo-first order model (Teuten et. al., 2007) in which the mass flux is proportional to the concentration difference across the aqueous boundary layer. Typically, Fickian diffusion is the rate limiting step (Sven et. al., 2019) and provide the fundament for description of pollutant release from microplastic surface (Yao and Weiyun, 2010), based on concentration gradient, release distance and biofilm growth (Lin et al., 1985). In this context, Fickian diffusion refers to the pollutant transport process in which the microplastic relaxation time ( $t_r$ ) is much greater than the characteristic medium diffusion time ( $t_d$ ) i.e  $t_r > t_d$ . A graphical illustration of possible desorption/release mechanism of pollutant from microplastic matrix is shown in Figure 7.

#### **4. Implication of microplastics-toxic chemical interaction**

There are many reports already on the abundance of microplastics in environment matrices viz water, soil and more recently air. As already established, their effects in the environment could be doubled by their interaction with toxic chemicals. In this section, the implications of that interaction are discussed under sections of environment and human health.

##### **4.1 Environment**

The environment literally means the surrounding; which extends from the elements of the microcosm, within every community to the cosmos of the atmosphere and universe. However, we shall only consider the implication of microplastics in three environmental media viz air, soil and water.

###### **4.1.1 Air**

The Earth's atmosphere is considered as air, in which living things live and breathe. Clean air happens to be the most important matter required by living organism for survival. Therefore, when air is contaminated, living organism is at risk of death. There are many studies available on air pollution regarding suspended particulate matter (SPM), but concerning the presence of suspended microplastics in air has gained little attention. Limited evidence is available on the transport of microplastics in air (Dris et. al., 2016; Dris et. al., 2017; Zhou et. al., 2017; Cai et. al., 2017; Kara et. al., 2018; Allen et. al., 2019; Liu et. al., 2019). These studies have identified fibrous microplastics (Figure 8) from atmospheric fallout at various concentrations both in indoor and outdoor air as well as in urban and remote areas. These findings suggest that humans may be at risk of potential exposure through inhalation or by contact through skin. Detailed review on available information regarding airborne microplastics has been conducted recently (Enyoh et. al., 2019b). However, researchers should explore how different microplastic types and shape, whether it is more of a film or fiber or fragment, affects the movement of microplastics in air. It might assume that a film with more surface area would travel farther than a fragment, but there is no evidence yet.

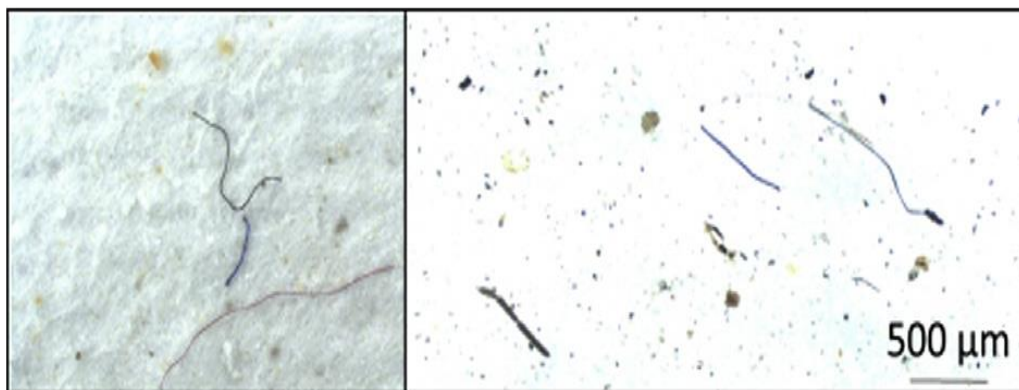


Figure 8. Fibrous microplastic observed in atmospheric fallout (Source: Gasperi et. al., 2018).

Generally, urban areas have higher distribution of atmospheric microplastics as reported by Dris and his colleagues in 2016, which isn't surprising as urban areas are known to experience high anthropogenic activities. From the urban areas, microplastics can be transported in air for more than 50 miles to remote areas. One study was recently published regarding air-borne microplastics in a remote mountain catchment (Allen et. al., 2019). The authors reported relative daily counts of 249 fragments, 73 films and 44 fibres per  $m^3$  in pristine mountain catchment (French Pyrenees), of which they came from neighbouring densely populated areas up to 95 km far north as revealed by air mass trajectory analysis (Allen et. al., 2019). A study by Dris et. al. (2017), investigated atmospheric fibers in indoor and outdoor air and revealed significant indoor concentrations of 1.0 to 60.0 fibers/ $m^3$  while lower concentrations of 0.3 to 1.5 fibers/ $m^3$  was reported for outdoor air. The suspended microplastics in indoor air later settled and accumulated in the indoor settled dust (190–670 fibers/mg), which can be re-suspended in air when the dust is perturbed.

Literature reviewed has shown that microplastics are present in air at varying concentrations controlled by the anthropogenic source and humans may be breathing it (Enyoh and Verla, 2019). This newly found exposure route of human to microplastics can be a call of concern, judging from the importance of air for human survival. Therefore, more detailed study on the distribution and potential ecological risk posed by airborne microplastics in the environment is required.

#### 4.1.2 Soil

One essential component of terrestrial ecosystems is soil and they experience strong pollution pressure. Microplastic contamination of soils is being increasingly documented, with potential consequences for soil biodiversity and function (Fuller and Gautam, 2016; Scheurer and Bigalke, 2018; Liu et al., 2018; Zhang et al., 2018a; Zhang and Liu 2018; Lv et al. 2019). However, the ecological impacts of microplastics in soils have been well reviewed (de Souza Machado et. al., 2018; Zhu et. al., 2019).

The impacts of soil microplastics can be on soil microorganisms, animals as well as plants growing on them. Reports suggest that the impact on soil microorganisms as well as antibiotic resistance genes (ARGs) may be positive or negative depending on particle type and concentrations. Liu et. al., (2017) found that PP particles at certain percentage in soil (7 % and 28 %) have positive effects on soil microbial activity while contrasting results was recorded for other plastic types at smaller concentrations (0.05–0.4 %) viz PA, polyester and PS (Awet et al. 2018; de Souza Machado et al. 2018). Furthermore, ARGs which has been gaining increasing attention recently due to their potential adverse effects on human health are affected by microplastics. Recently, the time of retention of ARGs in soil ecosystem has been shown to increase by the presence small concentration (0.1 %) of microplastics (particularly PP) (Sun et al. 2018). Conclusively the behavior/activity of soil microorganisms may vary according to plastic types, shape, size and concentration of microplastics present in the soil. However, these observations are still sketchy; therefore general conclusion cannot be drawn on the toxicity of microplastics in soil based on their type, shape and quantity. Also, studies have shown that soils microbial activities are affected toxic chemicals such as heavy metals in soil (Wyszkowska and Kucharski 2003; Wyszkowska and Wyszkowski, 2003; Verla et. al., 2017), therefore in tandem with microplastics may cause combined effects on soil microbial community. Research is

required to investigate how microplastics in synergy with toxic chemicals affect microbial movement or facilitates the transmission of ARGs in soil environment.

In terms of soil animals, there is only little information available on effects of microplastics pollution. Few studies have examined soil invertebrates, such as nematodes (Lei et al. 2018), collembolan (Zhu et al. 2018b; Ju et al. 2019), oligochaeta (e.g. earthworms) (Zhu et al. 2018c), and isopods (Kokalj et al., 2018). The toxicological effects of microplastics on these invertebrates are dependent on the size and particle concentration or level of exposure (Lei et al. 2018; Zhu et al. 2018c; Kim et al. 2019). Lei et al. (2018) examined the effects of different PS micro particle sizes (0.1, 0.5, 1.0, 2.0 and 5.0  $\mu\text{m}$ ) on nematode (*Caenorhabditis elegans*) for 3 days and found strongest toxicity of 1.0  $\mu\text{m}$ , due to the fact that nematodes easily accumulate moderate-sized microplastics in soil (Zhu et al., 2019). Also, the toxicity significantly downregulated the expression of *unc-17* and *unc-47* genes, reflecting damages to cholinergic and GABAergic neurons in nematodes (Lei et al., 2018). However, soil oligochaeta and lumbricidae are affected by the concentrations of microplastic particle in the soil medium.

Studies by Zhu et al. (2018c) and Huerta et al. (2016) demonstrated that high concentrations of PS (10 %) and PE (28–60 %) microplastics particle negatively affects and inhibits growth and survival of *Enchytraeus crypticus* (oligochaeta) and *Lumbricus terrestris* (earthworm) respectively in soil. Furthermore, biodegradable microplastics from starch-based biodegradable films in soil (1 %) had more effects on earthworm growth than conventional low density PE films (Qi et al., 2018). Zhu et al., (2019) pointed that this observation is possibly due to the main composition of biodegradable plastics (i.e Polyethylene terephthalate (PET) and polybutylene terephthalate), which might be more toxic than PE. Microplastics pollution in soil also affects soil collembolan as revealed by recent studies (Zhu et al. 2018b; Ju et al. 2019). For example, exposure of *Folsomia candida* in soil to PVC (0.1 %) and PE (0.1–1%) microplastics revealed significant inhibition of growth and reproduction of this animal (Zhu et al. 2018b; Ju et al. 2019). Also in both studies, gut bacterial community were significantly altered by the microplastic pollution in the soil. Only one study was found regarding the effects on microplastic pollution on soil isopod. Recent study by Kokalj et al., (2018) examined their behavior to feeding and how they reserve energy after 14 days of exposure to PE (0.4 %) microplastics and found no significant effects on the animal at the end of the experiment, thereby suggesting no or little hazardous effect of PE microplastics. Detailed investigation (could be for longer periods and varying concentrations of microplastics/toxic chemicals) of combined effects of different microplastics types and toxic chemicals on soil animals (invertebrates); growth or survival, feeding behavior and energy reserve should be carried out to gain more insight on the effects of the tandem interaction of microplastics-toxic chemicals.

The concern of microplastics polluted soil polluting plant is based on the tendency of plant accumulating them through uptake (Enyoh et al., 2019). This potential bioaccumulation can adversely affect the growth of the plant and food quality. Fluorescent microbeads can be used to investigate the possibility of plant uptake of microplastics (Zhu et al., 2019) while model such as bioaccumulation/concentration factors (BCF) can be used to assess the extent of accumulation. The hypothesis for the uptake is that plant cell wall and membrane barriers can be by-passed by small-sized microplastics (Zhu et al., 2019). Few evidences existed concerning uptake of nano (< 100nm) and micro (0.2  $\mu\text{m}$ ) plastics by plant (Bandmann et al. 2012; Li et al. 2019) and the effects on plant growth (Qi et al., 2018). Bandmann et al. (2012) demonstrated that through endocytosis, nano-scale fluorescent PS beads could enter tobacco cells. Li et al. (2019) assayed edible plants grown in China, found that fluorescent micro PS beads were transferred from the soil to the plants. These findings clearly showed the potential risk of consuming microplastic by human through plant web chain.

Meanwhile, their presence in plant can cause the plant to have a poor or stunted growth, effect which correlated strongly with biodegradable microplastics probably due to its composition (containing PoTSS i.e PET and polybutylene terephthalate) than conventional microplastics. Qi et al., (2018) found out that biodegradable microplastics have stronger negative effects on the growth of wheat and the fruit biomass than conventional PE microplastics. However, the toxicity of microplastic pollution (especially with adhered toxic chemicals) to plants should be investigated. Plants are known to bioaccumulate toxic chemicals, which have been used well in phytoremediation studies (Xiong 1998; Uwah et al., 2011; Ibe et al., 2017). However, the uptake of microplastics by plant could be beneficial for soil as plant is serving as a potential phytoremediator (Enyoh et al., 2019a). These concepts will be needed to be explored for clearer understanding of the potentiality of using plant as a phytoremediator of microplastics in soil.

### 4.1.3 Water

Microplastic pollution of aquatic ecosystem has been intensively studied as compared to soil ecosystem or in the atmosphere. Microplastic pollution is listed among the major perceived threats to biodiversity due to its abundance, durability and persistence in the marine environment (Gall and Thompson, 2015). The impacts of microplastics pollution in aquatic ecosystem has been extensively reviewed and documented (Gall and Thompson, 2015; Duis and Coors, 2016; GESAMP, 2016; UNEP, 2016; Carbery et. al., 2018; Smith et. al., 2018). These reviews provided a comprehensive documentation defining the current state of knowledge of microplastics: the provenance, fate, and externalities of their presence in our marine ecosystem and interaction with marine organisms. However, marine organisms generally interact with microplastic debris either via entanglement or ingestion. From reports, 220 species contaminated with microplastics was found to be through ingestion while 580 contaminated species was probably through entanglement (UNEP, 2016; Lusher et. al., 2017), totaling 800 species identified, including marine mammals, fish, invertebrates, and fish-eating birds. Detrimental effect of contamination includes particle accumulation in organism digestive tract and possible translocation from intestinal tract to the circulatory system or surrounding tissue (GESAMP, 2016; Lusher et. al., 2017; Smith et. al., 2018).

### 4.2 Toxicity to Human

Humans may ingest microplastics directly (via consumption of microplastic contaminated water, soil or salt) or indirectly via trophic transfer (e.g via consumption of microplastic contaminated seafood and plant) or inhaling airborne microplastics. The greatest exposure might be through seafood consumption, serving as major protein source and as the sea happens to be a hotspot for plastic debris pollution. Food and Agricultural Organization in their 2016 report on “the state of the world fisheries and aquaculture” reported that in 2015 alone, 6.7 % of human protein and 17% of animal protein consumed globally was from seafood (FAO, 2016). However, by implication of having fibrous microplastics in air from atmospheric fallout, they can enter the body through mouth or nose. Particularly fibrous microplastics that did not meet the criteria for airborne fibers i.e the length should be greater than 5 mm, with a diameter of less 3 mm and an aspect (length-to-diameter) ratio greater than 3 to 1 (WHO 1997).

Generally, the health effects depend on concentrations of microplastics exposed to. Currently, there is no accurate amount estimated for microplastics ingested by humans via food or air, due to data gap and limited evidence. However, an estimate for total microplastic intake by human annually via salt consumption was predicted by Yang et. al., (2015) to be at most 37 particles per individual while approximately 11,000 plastic particles was estimated to be consumed by a top European shellfish consumer annually (Van Cauwenberghe and Janssen, 2014; Yang et. al., 2015; Karami et al., 2017) while an estimate of 80 g per day was predicted for microplastics intake via plant (fruits and vegetable) (Enyoh et. al., 2019a). The implications of consuming microplastics are currently unknown; however impact may potentially be particle (via particle localization), chemical (with associated toxic chemicals) or microbial. The plausible effects of microplastics on human health have been critically discussed (see Wright and Kelly, 2017). Wright and Kelly (2017) critically assessed potential level of exposure of particle, chemical, and microbial hazards associated with microplastics to inform understanding of microplastics uptake, internalization, impacts, and potential adverse human health outcomes.

The particle toxicity occur when the critical mass of microplastics is localized and causing immune response from the body, of which the body can't do much about. There are no reports of particle toxicity of microplastics to human perhaps due to the ability of human disposing > 90 % of ingested plastics via faeces (Wright and Kelly, 2017; Smith et. al., 2018). How they are retained in or cleared from the body are depended on some factors which include size, shape, length, polymer type, and additive chemicals of microplastics (Lusher et. al., 2017). For example, in terms of length, longer fibrous microplastics have been reported to biopersist and resist being cleared from the lungs (Pimentel et. al., 1975; Warheit et. al., 2001) while shorter ones are easily cleared. The biopersistence can cause lung inflammation and potentially leads to secondary genotoxicity following the excessive and continuous formation of reactive oxygen species (ROS) (Gasperi et. al., 2018).

The general paradigm for chemical effects follows the fact that microplastics can sorp toxic chemicals such as heavy metals and HOCs on its pitted surface, thereby conferring exposure of humans to associated toxic chemicals. Detrimental pulmonary outcomes could then ensue following desorption of associated contaminants leading to primary genotoxicity, reproductive toxicity, carcinogenicity and mutagenicity (Linares et. al., 2015; Gasperi et. al.,

2018). For example, stable and unstable DNA lesions may arise after metabolism of fibrous-MP associated PAHs (Greim et. al., 2001). Few studies have assessed the relative contribution of microplastic exposure to additives or chemicals found in organisms, versus alternative exposure pathways (GESAMP, 2015; Smith et. al., 2018).

Microbial effects followed the ability of microorganisms forming biofilms on microplastics surface when exposed in aqueous medium. Harmful human pathogens such as strains of *Vibrio* spp have been isolated in formed biofilm on microplastics (Zettler et. al., 2013; Kirstein et. al., 2016). Also, as one of the plausible mechanism of toxic chemical transport by microplastics, formed biofilm can include heavy metals and HOCs. Richard (2016) found that biofilm growth assisted in metal (Ni, Al, Zn) accumulation on microplastics surface (LDPE and PLA). The relationship between and toxic chemicals can be problematic as microbes have the capacity to metabolize them (Vanhaecke et. al., 2006). This in turn can have knock on effects for the host, compromising immunity and stimulating inflammation in the body (Cho et. al., 2012). Oxidative stress and inflammation have a key role in the pathogenesis of inhaled pollutants, and also modify local conditions, which potentially influence the microbiome (Wright and Kelly, 2017).

## 5. Conclusions, Knowledge gaps and Future area of research

In the last 15 years, there has been an increased interest on microplastics pollution by researchers, which has brought about an expanding knowledge on the subject. Reports have confirmed that microplastics serve as a vector for toxic chemicals (heavy metals and HOCs) transport in the environment and when ingested with potential migration in the body. The conclusions from this study will be presented under different sections as presented in the review;

### *(1) Conclusions on quantified concentrations of toxic chemicals adhered on microplastics surface.*

- The toxic contaminant concentrations varied among locations, indicating that the contamination represents a local problem or the surroundings. Microplastic particles from heavily polluted areas contain higher levels than those from less polluted areas.
- Concentrations are controlled by discoloration of microplastic with yellowed (discolored) ones generally having higher concentration. Therefore, degradations stage of plastic plays an important role on concentration of sorped contaminant.
- Additives used in plastics are PoTSS and can migrate internally to plastic surface and externally from the plastic surface. Additives have the tendency to increase concentrations on toxic chemicals sorped from ambient environment.
- Generally, quantification of toxic chemicals from microplastic surface is mostly done using spectroscopic techniques following weak acid (e.g 10% HNO<sub>3</sub>) or aqua regia extraction for toxic metals while soxhlet assisted n-hexane, methanol (MeOH) or dichloromethane (DCM) extraction for organic pollutants.
- Twelve metals (Al, As, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, Ti, and Zn), one halogen (Br) and fifteen groups of organic pollutants (PAHs, PCBs, DDTs, HCHs, chlordanes, mirex, hexachlorobenzene, hopanes, PBDEs, PFC/PFA, aliphatic hydrocarbons, BPA, NPs and OPs) have generally been quantified from different locations up till now.
- Few studies have been reported concerning African marine environment (Ghana, Mozambique and South Africa) and none regarding Nigerian environment.

### *(2) Conclusions on adsorption and desorption mechanism*

- Currently, there are no accurate information on adsorption and desorption mechanisms of toxic chemicals onto/from microplastics. However, plausible adsorption mechanism include hydrophobic adsorption, biofilm growth assisted adsorption and additives.
- Refined models such as poly-parameter linear free energy relationship and novel film-pore mass transfer (FPMT) recently developed, was reported to be the best so far for studying adsorption mechanism of toxic chemicals.
- The following factors influences the desorption mechanism kinetics; Microplastic matrix: Composition/type, degradation, structure, binding energies, biofilm growth and surface properties; Release medium: pH, temperature, ligand concentration, concentration gradient, ionic strength and salinity; Pollutant: Solubility, redox state, interaction with matrix, charges and stability.



### (3) Conclusions on Implications

- Microplastics can be transported up to 95 km through air from their source to a new environment. Anthropogenic activities influences the amount of microplastics suspended in air.
- Microplastics can be suspended in indoor atmosphere and thus inhabitants may inhale microplastics from indoor air.
- Humans may inject microplastics directly (via consumption of microplastic contaminated water, soil or salt) or indirectly via trophic transfer (e.g via consumption of microplastic contaminated seafood and plant) or inhaling airborne microplastics.
- It is clear that marine and soil organisms can interact with microplastics via ingestion or entanglement and that laboratory experiments show that this can result in harm.
- Impact of microplastics on soil microbial community, animals and plant are depended on particle type, concentrations and size.
- Plants can accumulate microplastics from soil and laboratory experiments show that this can result in poor growth of the plant. Biodegradable microplastics have stronger negative effects on plant growth when compared to conventional microplastics.
- The implications of consuming microplastics by humans are currently unknown; however impact may potentially be particle (via particle localization), chemical (with associated toxic chemicals) or microbial (through biofilm formation).

### 5.1 Knowledge gaps and future area of research

- No study has tried to expressly determine the source of toxic chemicals adhered to microplastics whether it is from the environment or from the plastic itself. Therefore, research is needed to understand/know the sources of toxic chemicals found on microplastics, whether they came from additives or from ambient environment during particle exposure or they came from the two means working synergistically.
- There is need for further studies elucidating role of microplastics as sinks or sources of metals and HOCs in the environment
- Could toxic chemicals be transferred between microplastics particles and tissue organisms? Further study is required to evaluate the possibility of toxic chemical transfer between the plastic carrier particles and the tissues found in living organisms.
- How do anionic metal ion such as arsenic (As), selenium (Se), chromium VI [Cr(VI)], molybdenum (Mo) and boron (B), binds on surface of plastics ? Experimental studies are however required to unravel how aqueous anionic metal binds on surface of plastics.
- Microplastics are now reported in the atmosphere. How many toxic chemicals are carried by airborne microplastics? This information is the basis for a precise risk assessment.
- What is the extent of microplastic pollution and what type in terms of shape, size, length and colour is most abundant in soil?
- What are the risks of microplastics pollution in soil posed to plant? One study has studied effects on wheat growth. However, there are still more question to be answered such as the effects on many other plants (edible or non-edible), as well as how they are affected by microplastics types (in terms of color and shape).
- Uptake of microplastics by plant has been demonstrated (Li et. al., 2019) and as potential phytoremediator was discussed (Enyoh et. al., 2019a). However, the potentiality of using plant as a green cleaning method for microplastics in soil should be further explored for clearer understanding.
- It is already established that microplastics serve as vector for toxic chemicals transport in the environment. However, we need to get a better understanding about potential toxicity to plant, if plants while accumulating microplastics through uptake also accumulate toxic chemicals along.

### Conflicts of interest

The researchers declares no conflicts of interest regarding the publication of this manuscript

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