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(可降解)微塑料颗粒吸附有机污染物及对其生物有效性的影响*

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摘 要 微塑料是环境中一类不断增加的新兴污染物,工业生产活动以及日常生活是环境中微塑料的主要来源,同时农用塑料薄膜的残留对其也有贡献.鉴于不可降解塑料在环境中的持久性,作为传统塑料的替代品,可降解塑料的应用越来越多.然而,当前针对陆地系统微塑料的研究主要集中于不可降解材质的微塑料,针对可降解塑料作为微塑料来源的研究则十分匮乏.由于微塑料的憎水性和较大比表面积,进入环境中的微塑料能够通过分配作用和表面吸附作用大量吸附环境中的有机污染物从而改变被吸附物质的生物有效性;同时随着塑料的风化,生产过程中添加的大量助剂也会逐渐进入环境中.与不可降解微塑料相比,可降解微塑料的性质有很大不同,可降解微塑料与污染物的相互作用及对其生物有效性的影响也与不可降解微塑料不同.另外,可降解微塑料进入环境后,粒径及表面性质可在较短时间内产生变化,这些变化对可降解微塑料与有机污染物的相互作用及对所吸附有机污染物的生物有效性的影响有待研究.

关键词 可降解微塑料, 有机污染物, 吸附, 粒径, 生物有效性.

Adsorption of organic pollutants on (degradable) microplastics and the influences on their bioavailability

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Abstract: Microplastics are increasing emerging contaminants in the environment, and the industry production and daily life as well as debris of agriculture mulch are the main sources. As the substitute of traditional non-degradable plastics , the use of

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degradable plastics has increased continually in recent years, however, few researches have referred to degradable plastics as a potential source of microplastics. Research about microplastics in terrestrial environment has been primarily focused on non-degradable microplastics; it has been found that microplastics could adsorb large quantities of organic pollutants by partition and surface adsorption due to their hydrophobicity and large specific surface area, which further influences the bioavailability of these adsorbed pollutants. Besides, in response to the weathering effects, various additives added during the production of plastics would gradually enter the environment. Compared with non-degradable microplastics, degradable microplastics own varied properties which lead to different interaction patterns between microplastics and organic pollutants as well as influences on the bioavailability of pollutants. Besides, degradable microplastics would undergo changes of sizes and surface properties in relatively short periods after entering the environment; and these changes would have significant impacts on the adsorption and bioavailability of organic pollutants, which deserve intensive research.

Keywords: degradable microplastics, organic pollutants, adsorption, sizes, bioavailability.

随着塑料制品的大量使用,微米级甚至纳米级的塑料颗粒大量进入环境或在环境中产生.早在上个世纪 70 年代,就有学者在 Science 上撰文呼吁关注塑料碎片对生态环境的潜在危害[1-2].但是,直到本世纪微塑料颗粒污染的问题才得到科学家的广泛关注[3],2011 年,微塑料污染被联合国环境规划署(UNEP)列为全球要面对的一个新的问题和挑战.

微塑料广泛分布于海水、河流湖泊、沉积物等环境介质中,甚至在极地也有发现[4-6],同时环境中微塑料的含量呈现不断增加的趋势[7].在浮游生物、鱼类、鲸类等不同营养级生物体内均发现微塑料颗粒的存在[8-10],微塑料还能够沿着食物链向上传递到高营养级生物体内[11-13],在群落、个体水平上对生物体产生不利影响[14-18].同时微塑料对有机污染物有较强的吸附能力,并对有机污染物的生物有效性产生影响.

可降解塑料是塑料工业发展方向之一,是减轻当前不可降解塑料污染的解决方案.可降解塑料进入环境后短期内可产生大量的微塑料,一些可降解微塑料对有机污染物有很强的吸附能力,并可对环境中污染物的迁移转化产生影响;同时可降解微塑料在短期内可以发生显著的变化(表面结构及粒径),而这些变化可以影响微塑料对有机污染物的吸附,同时影响被吸附有机污染物的生物有效性,因此需要关注可降解微塑料的环境影响,尤其降解过程相关的环境学问题.

1 (可降解)微塑料来源(Source of (degradable) microplastics)

微塑料从化学组成上可以分为不可降解材质微塑料(non-degradable microplastic,不可降解微塑料)和可降解材质塑料(degradable microplastic,可降解微塑料)两大类(结构单元见图 1),不可降解微塑料主要材质有聚乙烯(PE)、聚丙烯(PP)、聚氯乙烯(PVC)、聚苯乙烯(PS)和聚对苯二甲酸乙二酯(PET)等;常见的可降解微塑料主要材质有聚乳酸(PLA)、聚羟基丁酸脂(PHA)和聚丁二酸丁二酯(PBS)等.

微塑料的来源可分为一次来源(primary source)和二次来源(secondary source).一次来源微塑料是指直接添加到化工及日化用品中的塑料颗粒和原料颗粒在加工使用过程中进入环境的塑料颗粒,如在新西兰某地和五大湖水体中所发现的磨砂颗粒[19];而废弃的塑料制品,如日用塑料制品、塑料包装、泡沫塑料等在机械、氧气和太阳辐射等作用下,进入环境后破碎裂解形成的微塑料则属于二次来源微塑料[20].

从微塑料具体来源来看,污水处理厂是微塑料显著的源和汇之一,来自生活生产的微塑料随着污水汇集到污水处理厂,大部分微塑料在处理过程中被除去,剩余部分通过出水输入到环境.根据对处理 650000 人生活污水的处理厂进出水中微塑料含量的研究发现,经过污水处理厂的沉淀絮凝等处理后 98.41% 的微塑料被除去,尽管去除率很高,其出水中每天也含有 6500 万个微塑料[21],另一项研究也得到相似的结论,发现污水处理厂出水中的微塑料含量比其受体水中含量高数倍[22],针对一条有污水处理厂出水排放的河流研究发现,污水出口下游的微塑料含量要远高于出水口上游微塑料的含量[23].其

他一些生活生产过程也是微塑料的来源,如使用洗衣机洗衣时每次可产生超过 1900 个纤维碎片[24],此外大气沉降、地表径流和生物噬咬海洋浮标设施也是微塑料的来源[25-27].

塑料薄膜残留则是另一个微塑料主要来源[28],以聚乙烯(PE)和聚氯乙烯(PVC)为材质的农用塑料薄膜在农业增产和土壤调节上发挥了重要作用,且用量持续增加[29],据统计,2014 年我国农用塑料薄膜的消耗量已高达 258 万吨,占全球农膜市场的 61%[30].据估测,当前世界范围内塑料薄膜使用后的回收率仅为 50%[31],而每年进入欧洲和北美农田中微塑料的量分别可达 6.3×10^4—4.3×10^5 t 和 4.4×10^4—3.0×10^5 t[32].传统农用薄膜自然环境下难以完全降解,PE 薄膜在土壤中 8.5 年依然保持基本形态完整,造成了塑料薄膜在土壤环境中不断积累[33].长期残留于土壤中的塑料薄膜则会在光照和氧气的作用下逐渐老化破碎成碎片,塑料碎片完全矿化则是一个极其缓慢的过程,最终导致薄膜源的微塑料逐渐在土壤中蓄积.

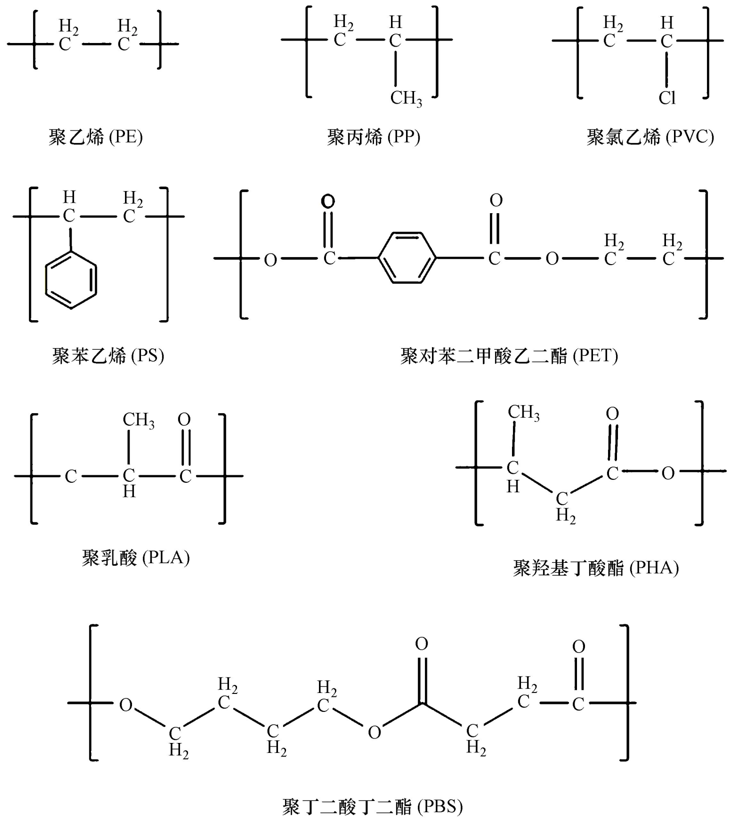

图 1　常见塑料结构单元

Fig.1　Chain element of several kinds of plastics

针对农膜残留的问题,有文章指出可降解塑料薄膜是未来农用塑料薄膜的发展方向[34].而当前可降解材质塑料薄膜也存在诸多问题,许多可降解薄膜并非可完全降解(降解率>90%),往往是不可降解塑料中掺入可降解塑料或者预氧化剂(pre-oxidant)等,使得塑料薄膜用毕后迅速解体为大量不可降解的塑料碎片(微塑料)[35-36],另外即便全部以可降解塑料制成塑料薄膜,其完全降解也需要一定的条件和时间,实际的环境往往不能满足其迅速完全矿化所需的条件,因此在相当长的时期内这些可降解塑料逐步缓慢降解,以微塑料的形式存在于土壤中.

2　(可降解)微塑料与有机污染物相互作用(Interaction between (degradable) microplastics and organic pollutants)

2.1　微塑料吸附有机污染物

微塑料具有较大的比表面积和较强的疏水性,因而对有机污染物有较强的吸附作用,针对水体中微塑料的调查发现微塑料上有多种有机污染物检出[37-39].微塑料吸附有机污染物受微塑料材质的影响,同

时有机污染物的特性对吸附也有较大的影响.

对不可降解微塑料的研究发现,微塑料对多环芳烃(PAHs)、多氯联苯(PCBs)、有机氯农药(OCPs)等污染物均表现出较强的吸附能力,有机污染物的分配系数高达 10^4—10^6 L·kg^{-1}[40-41],同时对离子型化合物及重金属离子也有一定的吸附能力[42-43].软质(玻璃化温度 T_g 较低,链段活动性较强)的塑料如 PP、PE 等对有机污染物有较强的吸附能力且吸附等温线多呈现线性,原因在于 PE 和 PP 的玻璃化温度较低,常温下呈软质的橡胶态,有机污染物较容易以分配作用的方式进入微塑料基质,因而吸附等温线呈线性且表现出较强的吸附能力;硬质塑料如 PS 等也能吸附一定量的 PCBs,因为 PCBs 能够与 PS 表面的结构发生 π-π 电子作用[44].另外离子型化合物和重金属的吸附研究则发现表面官能团可能对微塑料吸附污染物有一定的作用,对 3 种材质微塑料(PVC、PE、PP)吸附全氟辛烷磺酸(PFOS)和全氟辛基磺酰胺(PFOA)的研究发现,硬质塑料 PVC 吸附两种物质的能力要高于 PE 和 PP,作者推测 PVC 表面的极性基团能够与两种物质发生作用,因而呈现出较强的吸附能力[42],针对模拟塑料在河岸吸附壬基酚的研究也有类似结果[45].针对新鲜和海滩老化的同种材质微塑料吸附污染物的研究发现,老化的塑料相比新鲜的塑料吸附能力更强[46],这可能是老化作用使得微塑料表面的极性官能团增加,使得表面极性作用引起的吸附增加所致.同时发现,PS 微塑料颗粒对海水中非邻位 PCBs 的吸附能力高于邻位 PCBs,这是由于邻位取代氯原子破坏了 PCBs 平面性,导致 π-π 电子作用下降[44].

关于可降解微塑料吸附有机污染物的研究则是空白,可降解微塑料有着与不可降解微塑料不同的结构和性质,同时其短期内能够产生显著的变化,与有机污染物的作用情况也与传统塑料不尽相同.本课题组针对可降解微塑料的研究表明,三种可降解微塑料(PLA、PHA、PBS,300—500 μm)对有机污染物的吸附是一个缓慢的过程,平衡所需时间长达数 10 d.玻璃化温度较低的微塑料(PBS),对菲有很强的吸附能力($K_d = 10^4$ L·kg^{-1}),其吸附有机污染物菲的主要机制为分配作用,对吸附后的微塑料进行解吸,解吸滞后因子接近于 0,无明显滞后.同时针对加速老化后的可降解微塑料吸附行为进行研究,发现 PLA 材质微塑料老化后对菲的吸附能力显著增加(12 倍),玻璃化温度及表面结构改变则是可能的原因.这表明可降解微塑料进入环境后能够大量吸附环境中有机污染物,同时老化降解的过程可能加剧这一趋势,因此有必要加强可降解微塑料吸附污染物以及降解过程与有机污染物作用的研究.

2.2 微塑料向环境中释放有机污染物

微塑料从环境中吸附有机污染物的同时,还会向环境中释放污染物.塑料制品在生产过程中往往会添加大量的阻燃剂、塑化剂、颜料等助剂[47],使得进入环境的微塑料中含有这些添加剂,如针对韩国及亚太海岸的研究在发泡聚苯乙烯(EPS)残骸及微塑料中广泛检出较高浓度的六溴环十二烷(HBCDs)[48].风化破碎过程则会使这些助剂逐渐进入到环境,例如,Staniszewska 等针对特定流域的研究发现,塑料添加剂的释放是导致该流域内双酚类物质及壬基酚类物质含量升高的原因[49];对大量使用的 EPS 塑料的研究发现,EPS 塑料进入环境后所含 HBCDs 会逐渐释放出来,随着粒径的减小以及风化作用的侵蚀释放速率则会大大加快.根据既往针对 HBCDs 的研究,环境中 HBCDs 的能够在生物体内发生显著的蓄积[50-51].

在塑料薄膜进入土壤环境后,其包含的大量助剂(部分 PVC 中邻苯二甲酸酯(PAEs)含量高达 35%—40%)也会很快进入的土壤环境中[52-53],针对我国 14 个省 31 个地区的研究发现,农用塑料薄膜残留是土壤中 PAEs 类物质含量增加的直接原因.不回收塑料薄膜可使土壤中 PAEs 的含量从回收对照的 2 mg·kg^{-1}上升至 5.5—6.6 mg·kg^{-1},其中以邻苯二甲酸二异辛酯(DEHPs)为主,占 71.5%以上[54].而 PAEs 及其代谢产物属于环境内分泌干扰物,对人体具有生殖发育影响、胚胎毒性[55]和致癌毒性(如邻苯二甲酸丁苄酯(BBP)、DEHP)[56].

微塑料还会向环境中释放其携带的其他有害物质,例如环境中残留大量以含铅化合物作稳定剂生产的 PVC 制品,随着老化的进行,所含的铅则会逐渐释放到环境中[57];另外,生产塑料的单体和原料在塑料中也有相当的含量,这些物质在环境中也会逐渐进入环境中,如 PVC 中含有氯化氢,聚苯乙烯中含有苯乙烯的单体和低聚体,这些物质都会随着聚氯乙烯和聚苯乙烯的老化逐渐释放的环境中[58].

针对可降解塑料的研究发现可降解微塑料本身含有的以及降解产生的单体和低聚体也会逐渐释放到环境中,这些低聚体会对土壤生物产生毒害作用;针对 PBS 和 PLA 降解产物对作物生长影响的研究发

现,PBS 降解后的产物对辣椒和西红柿的生长产生了显著的抑制[59].而可降解塑料 DF04P(一种基于玉米淀粉的可降解塑料)薄膜降解后,则会使土壤 pH 值由 7.91 上升到 8.29,进而对土壤环境产生不利影响[60].

3 (可降解)微塑料对污染物生物有效性的影响(Impacts of (degradable) microplastics on the bioavailability of organic pollutants)

微塑料不仅能够吸附有机污染物,而且会对有机污染物的生物有效性造成影响.解吸是决定吸附态有机污染物流动性和生物可利用性的基础过程.对于土壤等地质吸附剂以及人造碳质吸附剂(纳米碳管及生物炭)的研究表明,解吸并不能按照吸附的相反过程可逆发生,称为吸附的不可逆性或者解吸的滞后性,形成锁定态残留,这大大降低了吸附态污染物的流动性和生物有效性[61].以往的研究表明,表面结构及纳米微孔是造成其解吸滞后的关键微观结构要素,解吸滞后性还随着污染物分子体积及憎水性而增加[62-64].目前关于微塑料颗粒是否可对污染物造成锁定尚未见报道.

对于被吸附的有机污染物生物有效性的研究尚缺乏,多数研究针对水生生物进行.Bakir 等研究了模拟消化液对吸附在微塑料(PE、PVC,200—250 μm)上的有机污染物(PFOA、PHE、DDT、DEHP)的解吸影响,发现与水溶液相比,模拟消化液可以促进微塑料上 4 种污染物的解吸[65],这表明着携带着有机污染物的微塑料进入生物体消化道后,所携带的有机污染物可以快速地从微塑料上解吸下来而被生物体吸收.针对斑马鱼的研究则发现,纳米 PP 颗粒的存在会导致双酚 A(BPA)对斑马鱼的神经毒性增加[66].Besseling 等发现向沉积物中添加 PS 颗粒(400—1300 μm)后,随着添加量的增加,海蚯蚓对 19 种 PCBs 的富集先增加后下降.推测可能的原因是当微塑料添加量低于一定浓度时,蚯蚓摄取大量微塑料,在消化过程中微塑料上吸附的大量 PCBs 解吸下来并被蚯蚓吸收导致富集量增加;而随着微塑料添加量的增加,沉积物中大量微塑料影响了海蚯蚓的生理活动,使得摄食的微塑料减少,进而导致对 PCBs 的富集量降低[67].同时,针对日化品中塑料珠(PE)对鱼富集多溴联苯醚(PBDE)影响的研究发现,塑料珠的添加可以增加低溴代 BDE 在鱼体内的富集;相同条件下,塑料珠对高溴代 BDE 的生物富集特性则没有显著的影响,研究人员推测是高溴代阻燃就对塑料珠的亲和能力较强难以解吸下来,而对鱼富集高溴代 BDE 没有显著影响[68].

相对于实验室研究,理论推导则指出添加微塑料可以减少生物体从环境中富集有机污染物.一项运用热力学方法评价微塑料对生物体富集有机污染物影响的研究表明,微塑料的存在有助于降低生物对憎水性有机污染物(K_{ow}>5)吸收[69];另一项模型研究也认为 PE 等与有机污染物亲和能力较强的微塑料可以降低生物体对有机污染物的富集,能够起到清洁的作用[70].

李冰研究了向土壤中添加不同粒径 EPS 颗粒后蚯蚓对其所含 HBCDs 的富集情况,发现 HBCDs 能够在蚯蚓体内富集,并且富集系数受 EPS 粒径影响,一方面 EPS 颗粒中的 HBCDs 能够向土壤中释放进而被蚯蚓富集,此外蚯蚓也能够通过直接吞食 EPS 颗粒,后经消化液的解吸作用而富集 HBCDs[71].

与不可降解微塑料相比,部分可降解微塑料有较强的吸附能力,同时解吸滞后不显著,使得可降解微塑料可以作为有机污染物转运载体,从环境中富集有机污染物,然后经消化作用解吸而被生物所吸收,具有潜在的环境风险.另外,可降解微塑料进入自然界后较短时期(相对与不可降解塑料)内即可出现粒径逐渐减小的变化过程.粒径的减小一方面可以加速微塑料对有机污染物的吸附;另一方面粒径的不同能显著改变微塑料的环境影响,例如针对蚯蚓(*Lumbricus*)的研究发现,其吞食的微塑料粒径多数小于 50 μm,即大粒径的微塑料很少或不被吞食[18].大粒径微塑料吸附周围环境中的污染物而降低有机污染物的生物有效性,即上文提及的清洁作用;而小粒径的微塑料大量吸附有机污染物后可经由吞食作用进入生物消化道,在消化道中被吸附的有机污染物解吸而被生物体吸收进而提高生物体对有机污染物的富集效应.课题组针对不同粒径 PBS 塑料对蚯蚓富集 HBCDs 的影响的研究则反映了该现象.另外针对不同粒径 PS 塑料对龙虾富集 PCBs 的研究也发现,大粒径 PS 微塑料(500—600 μm)由于不能被龙虾吞食且可从环境中吸附 PCBs 起到降低龙虾富集 PCBs 的作用,而小粒径 PS 微塑料(6 μm)由于可被龙虾吞食则增加了龙虾对 PCBs 的富集[72].而针对土壤中残留农膜的研究则发现,大尺寸(20 × 20 mm)的农膜残留能够降低土壤的饱和导水率(saturated hydraulic conductivity),对土壤微生物群落产生不利影响[73];小粒径塑料颗粒(PP, 180 μm)的添加则对土壤有一定的益处,小粒径塑料颗粒能较强地吸附

土壤中有机污染物则是可能的原因[74].可降解微塑料进入环境后在相对短时期内可发生降解而改变粒径,不同粒径可降解微塑料对有机污染物和生物有效性的影响则有很大的差异,因此针对可降解微塑料不同降解阶段对环境中有机污染物的影响需要深入研究.

4 展望及拟开展研究(Outlook and future research)

当前许多研究集中于不可降解微塑料,针对可降解微塑料的研究则十分匮乏.首先,针对可降解微塑料吸附有机污染物的研究较少,可降解微塑料的性质与传统塑料有很大的不同,部分可降解塑料的玻璃化温度较低,有机污染物进入其内部较容易,使可降解微塑料对有机污染物有较大的吸附容量;同时可降解微塑料表面富含极性官能团,极性官能团的存在使得污染物能够与微塑料表面发生极性作用,进而增加可降解微塑料对有机污染物的吸附.另外,可降解微塑料进入环境后粒径会逐渐减小,不同粒径的微塑料对有机污染物的吸附不同,粒径的降低及老化过程能够增加一些可降解微塑料吸附能力;更重要的是粒径的变化对微塑料所吸附有机污染物的生物有效性的影响不同,由于可降解微塑料粒径变化更明显,粒径的影响在可降解微塑料上更加突出.因此,有必要对可降解微塑料吸附有机污染物进行研究,同时需要加大关注可降解微塑料的环境影响在其降解过程中的变化情况.因此,课题组拟对下述问题开展研究.

(1)阐明不同结构的典型微塑料颗粒在我国主要类型土壤中经长期作用后结构上的变化,重点关注微塑料颗粒与土壤微生物群落的相互作用机制;

(2)探索不同类型微塑料颗粒对不同结构目标化合物的吸附规律及微观机理;

(3)认识不同来源(内源性与外源性)污染物从不同结构微塑料颗粒中的解吸或释放的规律与锁定机理,为评价微塑料颗粒吸附态污染物的风险提供科学基础;

(4)揭示微塑料颗粒对土壤中目标有机污染物蚯蚓富集生物有效性的影响规律,评价微塑料颗粒吸附态污染物的生态风险.

参考文献(References)

[1] CARPENTER E J, SMITH K L. Plastics on the Sargasso Sea Surface[J]. Science, 1972, 175(4027): 1240-1241.
[2] COLTON J B, BURNS B R, KNAPP F D. Plastic particles in surface waters of the northwestern atlantic[J]. Science, 1974, 185(4150): 491-497.
[3] 周倩, 章海波, 李远, 等. 海岸环境中微塑料污染及其生态效应研究进展[J]. 科学通报, 2015, 60(33): 3210-3220.
ZHOU Q, ZHANG H B, LI Y et al. Progress in research about contamination and bio-effects of microplastics in coastal environment[J]. Chinese Science Bulletin, 2015, 60(33): 3210-3220(in Chinese).
[4] OBBARD R W, SADRI S, WONG Y Q, et al. Global warming releases microplastic legacy frozen in Arctic Sea ice[J]. Earths Future, 2014, 2(6): 315-320.
[5] EERKESM D, THOMPSON R C, ALDRIDGE D C. Microplastics in freshwater systems: A review of the emerging threats, identification of knowledge gaps and prioritisation of research needs[J]. Water Research, 2015, 75: 63-82.
[6] BARNES D K A, GALGANI F, THOMPSON R C, et al. Accumulation and fragmentation of plastic debris in global environments[J]. Philosophical Transactions of the Royal Society of London, 2009, 364(1526): 1985-1998.
[7] GOLDSTEIN M C, ROSENBERG M, CHENG L. Increased oceanic microplastic debris enhances oviposition in an endemic pelagic insect[J]. Biology Letters, 2012, 8(5): 817-820.
[8] LUSHER A L, HERNANDEZMILIAN G, O'BRIEN J, et al. Microplastic and macroplastic ingestion by a deep diving, oceanic cetacean: The True's beaked whale Mesoplodon mirus[J]. Environmental Pollution, 2015, 199: 185-191.
[9] COLLARD F, GILBERT B, EPPE G, et al. Detection of anthropogenic particles in fish stomachs: An isolation method adapted to identification by raman spectroscopy[J]. Archives of Environmental Contamination & Toxicology, 2015, 69(3): 331-339.
[10] REHSE S, KLOAS W, ZARFL C. Short-term exposure with high concentrations of pristine microplastic particles leads to immobilisation of *Daphnia magna*[J]. Chemosphere, 2016, 153: 91-99.
[11] FARRELL P, NELSON K. Trophic level transfer of microplastic: *Mytilus edulis* (L.) to *Carcinus maenas* (L.)[J]. Environmental Pollution, 2013, 177: 1-3.
[12] FOSSI M C, PANTI C, GUERRANTI C, et al. Are baleen whales exposed to the threat of microplastics? A case study of the Mediterranean fin whale (*Balaenoptera physalus*)[J]. Marine Pollution Bulletin, 2012, 64(11): 2374-2379.
[13] WRIGHT S L, THOMPSON R C, GALLOWAY T S. The physical impacts of microplastics on marine organisms: A review[J]. Environmental Pollution, 2013, 178(1): 483-492.
[14] ROCHMAN C M, BROWNE M A, HALPERN B S, et al. Policy: Classify plastic waste as hazardous[J]. Nature, 2013, 494(7436): 169-171.
[15] LONNSTEDT O M, EKLOV P. Environmentally relevant concentrations of microplastic particles influence larval fish ecology[J]. Science,

2016, 352(6290): 1213-1216.

[16] SUSSARELLU R, SUQUET M, THOMAS Y, et al. Oyster reproduction is affected by exposure to polystyrene microplastics[J]. Proceedings of the National Academy of Sciences of the United States of America, 2016, 113(9): 2430-2435.

[17] RAMOS L, BERENSTEIN G, HUGHES E A, et al. Polyethylene film incorporation into the horticultural soil of small periurban production units in Argentina[J]. Science of the Total Environment, 2015, 523: 74-81.

[18] HUERTA L E, GERTSEN H, GOOREN H, et al. Microplastics in the terrestrial ecosystem: Implications for lumbricus terrestris (*Oligochaeta*, *Lumbricidae*)[J]. Environmental Science & Technology, 2016, 50(5): 2685-2691.

[19] ERIKSEN M, MASON S, WILSON S, et al. Microplastic pollution in the surface waters of the Laurentian Great Lakes[J]. Marine Pollution Bulletin, 2013, 77(1-2): 177-182.

[20] DRIS R, GASPERI J, ROCHER V, et al. Microplastic contamination in an urban area: A case study in Greater Paris[J]. Environmental Chemistry, 2015, 12(5): 592-599.

[21] MURPHY F, EWINS C, CARBONNIER F, et al. Wastewater treatment works (WwTW) as a source of microplastics in the aquatic environment[J]. Environmental Science & Technology, 2016, 50(11): 5800-5808.

[22] TALVITIE J, HEINONEN M, PAAKKONEN J P, et al. Do wastewater treatment plants act as a potential point source of microplastics? Preliminary study in the coastal Gulf of Finland, Baltic Sea[J]. Water Science and Technology, 2015, 72(9): 1495-1504.

[23] MCCORMICK A, HOELLEIN T J, MASON S A, et al. Microplastic is an abundant and distinct microbial habitat in an urban river[J]. Environmental Science & Technology, 2014, 48(20): 11863-11871.

[24] BROWNE M A, CRUMP P, NIVEN S J, et al. Accumulation of microplastic on shorelines woldwide: Sources and sinks[J]. Environmental Science & Technology, 2011, 45(21): 9175-9179.

[25] DRIS R, GASPERI J, SAAD M, et al. Synthetic fibers in atmospheric fallout: A source of microplastics in the environment?[J]. Marine Pollution Bulletin, 2016, 104(1-2): 290-293.

[26] MOORE C J, Lattin G L, ZELLERSAF. Quantity and type of plastic debris flowing from two urban rivers to coastal waters and beaches of Southern California [J]. Journal of Integrated Coastal Zone Management, 2011, 11: 65-73.

[27] DAVIDSON T M. Boring crustaceans damage polystyrene floats under docks polluting marine waters with microplastic[J]. Marine Pollution Bulletin, 2012, 64(9): 1821-1828.

[28] BLäSING M, AMELUNG W. Plastics in soil: Analytical methods and possible sources[J]. Science of the Total Environment, 2018, 612: 422-435.

[29] KYRIKOU I, BRIASSOULIS D. Biodegradation of agricultural plastic films: A critical review[J]. Journal of Polymers and the Environment, 2007, 15(3): 227-227.

[30] 国家统计局农村社会经济调查司. 中国农村统计年鉴[M]. 北京: 中国统计出版社, 2015.
Department of rural social and economic investigation of the National Bureau of Statistics.China Rural Statistical Yearbook[M]: Beijing: China Statistics Press, 2015(in Chinese).

[31] KASIRAJAN S, NGOUAJIO M. Polyethylene and biodegradable mulches for agricultural applications: A review[J]. Agronomy for Sustainable Development, 2012, 32(2): 501-529.

[32] NIZZETTO L, LANGAAS S, FUTTER M. Pollution: Do microplastics spill on to farm soils?[J]. Nature, 2016, 537(7621): 488-488.

[33] BRIASSOULIS D, BABOU E, HISKAKIS M, et al. Analysis of long-term degradation behaviour of polyethylene mulching films with pro-oxidants under real cultivation and soil burial conditions[J]. Environmental Science & Pollution Research International, 2015, 22(4): 2584-2598.

[34] SINTIM H Y, FLURY M. Is biodegradable plastic mulch the solution to agriculture's plastic problem?[J]. Environmental Science &Technology, 2017, 51(3): 1068-1069.

[35] BRODHAGEN M, PEYRON M, MILES C, et al. Biodegradable plastic agricultural mulches and key features of microbial degradation[J]. Applied Microbiology and Biotechnology, 2015, 99(3): 1039-1056.

[36] STLOUKAL P, VERNEY V, COMMEREUC S, et al. Assessment of the interrelation between photooxidation and biodegradation of selected polyesters after artificial weathering[J]. Chemosphere, 2012, 88(10): 1214-1219.

[37] MATO Y, ISOBE T, TAKADA H, et al. Plastic resin pellets as a transport medium for toxic chemicals in the marine environment[J]. Environmental Science & Technology, 2001, 35(2): 318-324.

[38] ENDO S, TAKIZAWA R, OKUDA K, et al. Concentration of polychlorinated biphenyls (PCBs) in beached resin pellets: Variability among individual particles and regional differences[J]. Marine Pollution Bulletin, 2005, 50(10): 1103-1114.

[39] FISNER M, TANIGUCHI S, MAJER A P, et al. Concentration and composition of polycyclic aromatic hydrocarbons (PAHs) in plastic pellets: Implications for small-scale diagnostic and environmental monitoring[J]. Marine Pollution Bulletin, 2013, 76(1-2): 349-354.

[40] KARAPANAGIOTI H K, KLONTZA I. Testing phenanthrene distribution properties of virgin plastic pellets and plastic eroded pellets found on Lesvos island beaches (Greece)[J]. Marine Environmental Research, 2008, 65(4): 283-290.

[41] ROCHMAN C M, HOH E, HENTSCHEL B T, et al. Long-Term field measurement of sorption of organic contaminants to five types of plastic pellets: Implications for plastic marine debris[J]. Environmental Science & Technology, 2013, 47(3): 1646-1654.

[42] WANG F, SHIH K M, LI X Y. The partition behavior of perfluorooctanesulfonate (PFOS) and perfluorooctanesulfonamide (FOSA) on microplastics[J]. Chemosphere, 2015, 119: 841-847.

[43] HOLMES L A, TURNER A, THOMPSON R C. Adsorption of trace metals to plastic resin pellets in the marine environment[J]. Environmental Pollution, 2012, 160: 42-48.

[44] VELZEBOER I, KWADIJK C, KOELMANS A A. Strong sorption of pcbs to nanoplastics, microplastics, carbon nanotubes, and fullerenes [J]. Environmental Science & Technology, 2014, 48(9): 4869-4876.

[45] HANKETT J M, COLLIN W R, YANG P, et al. Low-volatility model demonstrates humidity affects environmental toxin deposition on plastics at a molecular level[J]. Environmental Science & Technology, 2016, 50(3): 1304-1312.

[46] PAGES P, CARRASCO F, SAURINA J, et al. FTIR and DSC study of HDPE structural changes and mechanical properties variation when exposed to weathering aging during Canadian winter[J]. Journal of Applied Polymer Science, 1996, 60(2): 153-159.

[47] CORCORAN P L, NORRIS T, CECCANESE T, et al. Hidden plastics of Lake Ontario, Canada and their potential preservation in the sediment record[J]. Environmental Pollution, 2015, 204: 17-25.

[48] JANG M, SHIM W J, HAN G M, et al. Widespread detection of a brominated flame retardant, hexabromocyclododecane, in expanded polystyrene marine debris and microplastics from South Korea and the Asia-Pacific coastal region[J]. Environmental Pollution, 2017, 231: 785-794.

[49] STANISZEWSKA M, GRACA B, NEHRING I. The fate of bisphenol A, 4-tert-octylphenol and 4-nonylphenol leached from plastic debris into marine water - experimental studies on biodegradation and sorption on suspended particulate matter and nano-TiO_2[J]. Chemosphere, 2016, 145: 535-542.

[50] LI B, ZHU H K, SUN H W, et al. Effects of the amendment of biochars and carbon nanotubes on the bioavailability of hexabromocyclododecanes (HBCDs) in soil to ecologically different species of earthworms [J]. Environmental Pollution, 2017, 222: 191-200.

[51] LI B, YAO T Q, SUN H W, et al. Diastereomer- and enantiomer-specific accumulation, depuration, bioisomerization, and metabolism of hexabromocyclododecanes (HBCDs) in two ecologically different species of earthworms[J]. Science of the Total Environment, 2016, 542: 427-434.

[52] WANG J, LV S, ZHANG M, et al. Effects of plastic film residues on occurrence of phthalates and microbial activity in soils[J]. Chemosphere, 2016, 151: 171-177.

[53] HUANG S H, LI J, JIN S. Effects of different mulch films on peanut yield and paes pollution in soils[J]. Crops, 2015(3): 139 -141.

[54] CHEN Y S, WU C, ZHANG H, et al. Empirical estimation of pollution load and contamination levels of phthalate esters in agricultural soils from plastic film mulching in China[J]. Environmental Earth Sciences, 2013, 70(1): 239-247.

[55] WITTASSEK M, KOCH H M, ANGERER J, et al. Assessing exposure to phthalates - the human biomonitoring approach[J]. Molecular Nutrition & Food Research, 2011, 55(1): 7-31.

[56] BUI T T, ALVES A, PALM-COUSINS A, et al. Estimating uptake of phthalate ester metabolites into the human nail plate using pharmacokinetic modelling[J]. Environment International, 2017, 100: 148-155.

[57] NAKASHIMA E, ISOBE A, KAKO S, et al. The potential of oceanic transport and onshore leaching of additive-derived lead by marine macro-plastic debris[J]. Marine Pollution Bulletin, 2016, 107(1): 333-339.

[58] GREEN D S, BOOTS B, SIGWART J, et al. Effects of conventional and biodegradable microplastics on a marine ecosystem engineer (Arenicola marina) and sediment nutrient cycling[J]. Environmental Pollution, 2016, 208: 426-434.

[59] KIM M N, SHIN J H, IM S S. Effect of Poly(l-Lactide) and Poly(Butylene Succinate) on the growth of red pepper and tomato[J]. Journal of Polymers & the Environment, 2003, 11(3): 101-105.

[60] BETTAS A G, TOSIN M, BARBALE M, et al.Biodegradation of plastics in soil and effects on nitrification activity: A laboratory approach [J]. Frontiers in Microbiology, 2014,5:710-717.

[61] CABRERA A, COX L, SPOKAS K, et al. Influence of biochar amendments on the sorption – desorption of aminocyclopyrachlor, bentazone and pyraclostrobin pesticides to an agricultural soil[J]. Science of the Total Environment, 2014, s 470 – 471(2): 438-443.

[62] WU W L, SUN H W. Sorption-desorption hysteresis of phenanthrene - effect of nanopores, solute concentration, and salinity[J]. Chemosphere, 2010, 81(7): 961-967.

[63] XU X, SUN H W, SIMPSON M J. Concentration- and time-dependent sorption and desorption behavior of phenanthrene to geosorbents with varying organic matter composition[J]. Chemosphere, 2010, 79(8): 772-778.

[64] ZHOU Z L, SUN H W, ZHANG W. Desorption of polycyclic aromatic hydrocarbons from aged and unaged charcoals with and without modification of humic acids[J]. Environmental Pollution, 2010, 158(5): 1916-1921.

[65] BAKIR A, ROWLAND S J, THOMPSON R C. Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions[J]. Environmental Pollution, 2014, 185: 16-23.

[66] CHEN Q, YIN D, JIA Y, et al. Enhanced uptake of BPA in the presence of nanoplastics can lead to neurotoxic effects in adult zebrafish [J]. Science of the Total Environment, 2017, 609: 1312-1321.

[67] BESSELING E, WEGNER A, FOEKEMA E M, et al. Effects of microplastic on fitness and pcb bioaccumulation by the lugworm arenicola marina (l.)[J]. Environmental Science & Technology, 2013, 47(1): 593-600.

[68] WARDROP P, SHIMETA J, NUGEGODA D, et al. Chemical pollutants sorbed to ingested microbeads from personal care products accumulate in fish[J]. Environmental Science & Technology, 2016, 50(7): 4037-4044.

[69] GOUIN T, ROCHE N, LOHMANN R, et al. A thermodynamic approach for assessing the environmental exposure of chemicals absorbed to microplastic[J]. Environmental Science & Technology, 2011, 45(4): 1466-1472.

[70] KOELMANS A A, BESSELING E, WEGNER A, et al. Plastic as a carrier of pops to aquatic organisms: A model analysis[J]. Environmental Science & Technology, 2013, 47(14): 7812-7820.

[71] 李冰. 土壤中六溴环十二烷的生物有效性研究[D]. 天津:南开大学环境科学与工程学院, 2017.
LI B. Study on the bioavailability of hexabromocyclododecanes in soil[D]. Tianjin: College of Environmental Science and Engineering, Nankai University, 2017(in Chinese).

[72] DEVRIESE L I, WITTE B D, VETHAAK A D, et al. Bioaccumulation of PCBs from microplastics in Norway lobster (*Nephrops norvegicus*): An experimental study[J]. Chemosphere, 2017, 186: 10-16.

[73] WANG Z, LI X, SHI H, et al. Effects of residual plastic film on soil hydrodynamic parameters and soil structure[J]. Transactions of the Chinese Society for Agricultural Machinery, 2015, 46(5): 101-106.

[74] LIU H, YANG X, LIU G, et al. Response of soil dissolved organic matter to microplastic addition in Chinese loess soil[J]. Chemosphere, 2017, 185: 907-917.