科学通报 2016 年 第 61 卷 第 14 期：1604 ~ 1611
论 文
《中国科学》杂志社
SCIENCE CHINA PRESS

滨海潮滩土壤中微塑料的分离及其表面微观特征

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2015-09-29 收稿, 2015-12-13 修回, 2015-12-30 接受, 2016-03-29 网络版发表
中国科学院重点部署项目(KZZD-EW-14)和中国科学院战略先导专项(XDA11020402)资助

摘要 微塑料(<5 mm)作为海岸带地区的新型污染物正越来越受到关注. 本研究以我国河北省曹妃甸围填海区潮滩土壤为例, 采用自行改进设计的连续流动-气浮分离一体化装置, 有效分离和提取了潮滩土壤样品中微塑料, 并结合扫描电子显微镜-能谱仪(SEM-EDS)对微塑料表面的微观特性进行了表征. 研究结果表明, 供试土壤中微塑料丰度达到317 *n*/500 g(其中*n*表示微塑料个数), 平均粒径为1.56±0.63 mm, 其中<1 mm的微塑料占49.8%; 微塑料丰度上整体呈现随粒径变小而增加的趋势. 在土壤中分离到碎片、颗粒、纤维和薄膜四类微塑料, 其中, 黑色碎片类微塑料为首次报道的类型. 颗粒类微塑料丰度最大但平均粒径最小. 土壤中微塑料表面均有不同程度的风化痕迹, 具有不同形态和大小的微孔结构. 在部分微塑料中还发现其表面附着稳定的铁氧化物. 未来需要深入研究了解基于微塑料表面特性的污染物结合机制、生物积累与生态毒性, 尤其更需关注丰度较高、颗粒更细的<1 mm的这部分微塑料(MP1).

关键词 微塑料污染, 表面微形貌, 丰度, 连续流动-气浮分离, 海岸带土壤

塑料在日常生活中广泛应用, 但由于其难降解性, 在环境中长期残留, 并可进行远距离运输[1]. 环境中残留的塑料碎片或微塑料(<5 mm), 经过物理、化学风化作用会进一步裂解成更小颗粒[2]. 例如, 一个粒径为200 mm的塑料碎片可逐步碎裂成62500个粒径约为0.8 mm的微塑料[3]. 相比较于塑料碎片, 颗粒越小的微塑料其表面积越大, 更易吸附多氯联苯(PCBs)和多环芳烃(PAHs)等有机污染物[4,5]及重金属[6]. 同时, 这些小颗粒塑料易被海洋生物误食, 造成危害[1,7~10]. 因而, 海洋及海岸带环境中的微塑料污染正越来越受到关注[11].

环境样品中微塑料的分离提取是开展微塑料污染研究的关键. 目前, 水面漂浮微塑料主要通过过滤收集[12]; 沉积物或土壤等固体样品中微塑料的分离主要通过浮选分离, 或者直接通过密度分离的溶液浮选法[13~15], 或者利用向悬浊液中通气的气浮分离法[15~17]等. 但这些方法还存在步骤繁琐、回收率不稳定、提取效率不高等问题. 分离收集的微塑料样品需要进一步通过鉴定与表征, 以明确塑料的成分和特征. 其中, 表面形貌特征是微塑料研究的一项重要内容, 可为微塑料的鉴别、分类及其在环境中的分解过程研究提供重要的依据[6,18]. Corcoran等人[13]和Van Cauwenberghe等人[19]都利用扫描电子显微镜(SEM)观察沉积物样品中微塑料的形貌、轮廓及表面纹理特征; Eriksen等人[20]通过与能谱分析(EDS)相结合, 鉴别了表面的元素组成; Ashton等人[6]通过SEM-EDS鉴定出微塑料扁粒表面的灰化、裂化和粉化等老化特征. 此外, 为准确鉴定微塑料的成分及表观特征, 通

引用格式: 周倩, 章海波, 周阳, 等. 滨海潮滩土壤中微塑料的分离及其表面微观特征. 科学通报, 2016, 61: 1604–1611
Zhou Q, Zhang H B, Zhou Y, et al. Separation of microplastics from a coastal soil and their surface microscopic features (in Chinese). Chin Sci Bull, 2016, 61: 1604–1611, doi: 10.1360/N972015-01098

常会使用去离子水、盐酸、双氧水或酶消化制剂等溶液对微塑料表面进行清洗[15,20~22]. 但目前对不同清洗方法的适用性以及不同溶液对微塑料表面的影响尚未见报道.

本研究以我国北方曹妃甸围填海区潮滩土壤微塑料调查为例, 探讨建立了土壤样品中微塑料的分离方法, 区分了微塑料类型及其粒径, 测算了其丰度, 并结合前处理方法表征了滨海潮滩土壤中微塑料表面的形貌, 为我国滨海土壤、沉积物及海滨沙滩中微塑料的调查和研究提供方法学参考和基础数据信息.

1 材料与方法

1.1 供试土壤样品采集

供试土壤样品采自曹妃甸围填海区潮滩废弃盐场, 面积约为5000 m^2(图1). 场地内均匀分布着裸露的老化塑料管、以及零星散布的工程塑料编织袋等. 随机选择若干1 m×1 m正方形采样点, 采集表面约2 cm厚的土壤, 装入自封袋后带回实验室, 放置于清洁避光处, 在室温下风干.

1.2 微塑料回收率试验和供试土壤中微塑料的分离

在Nuelle等人[15]的简易浮选装置基础上, 改进设计了一套新的连续流动-气浮分离装置[23]. 该装置由液体存储、气浮溢流、筛分回收三部分组成, 各部分通过蠕动泵和导管联接, 实现了大体积固体样品的连续流动-浮选一体化. 在微塑料回收率试验上, 首先在野外采集的500 g清洁海沙中添加0.4573 g粒径为0.2~5.0 mm的聚乙烯、聚丙烯两种微塑料, 混合均匀后, 采用上述气浮装置和饱和氯化钠溶液进行分离, 设定浮选液流速为1.0 L/min, 微塑料回收率高达97%. 该回收率明显高于经典的密度分离法中39.8%的回收率[24], 也高于Zhu[17]采用淘洗管装置分离得到的回收率(最高为50%). 可见, 该装置及分离程序不仅操作简单、人工干预少, 而且分离效率高, 应该适用于土壤和沉积物中微塑料的分离.

本研究采用该装置进行供试土壤样品的气浮分离. 称取500 g土壤样品(干重计)用于微塑料浮选; 先用饱和氯化钠溶液浮选, 获得初步分离样品(约100 g), 然后再用饱和碘化钠溶液(密度为1.8 g/cm^3)进行浮选

图 1 采样区景观照片及浮选分离的微塑料

Figure 1 Photos of the landscape of the sampling site and the microplastics separated from the soil sample

分离，收集上清液，用真空抽滤装置过滤(碘化钠溶液可回收利用)和洗净盐分，将微塑料放入玻璃培养皿中，加盖风干．在放大镜或光学显微镜辅助下挑选微塑料，并按形貌和颜色进行分类、保存．通过上述浮选、分离、挑选过程，可以在该供试的曹妃甸土壤样品中分离到不同粒径的碎片、颗粒、纤维和薄膜4类微塑料．据上，可以认为用改进设计的连续流动-气浮分离装置及方法进行土壤或沉积物中微塑料的分离是可行的．

1.3 土壤中提取的微塑料表面酸清洗处理

从土壤中提取的微塑料样品，表面通常附着较多的细颗粒土壤或有机物质等．为了解和表征微塑料表面微形貌，本研究参考Eriksen等人[20]和Nuelle等人[15]的方法，选用盐酸对微塑料样品表面进行清洗处理．首先用2 mol/L盐酸溶液对微塑料浸泡24 h，然后超声处理(500 W，15 min)，再用去离子水冲洗，室温下风干．同时，以仅用去离子水清洗为对照处理．

1.4 微塑料计数和形貌鉴定及表征

对于浮选分离后的微塑料计数与粒径测量，先将样品进行单层平铺拍照，然后利用Nano Measurer 1.2软件处理照片，进行计数，其粒径以微塑料的最长一边的长度测量．微观形貌上，运用扫描电子显微镜(Hitachi S-4800型冷场发射扫描电子显微镜)进行观察鉴定，并结合能谱仪(HORIBA EX-350型能量分散型X射线分析装置)分析所选取的表面微域的元素组成．

2 结果与讨论

2.1 微塑料类型和丰度

供试土壤中存在碎片、颗粒、纤维和薄膜4种不同形貌的微塑料(表1)，总体丰度约为317 *n*/500 g(干重计)．其中，颗粒类微塑料数量最多(图2(a))，约占总数的3/4；其次是碎片类微塑料，占1/5；而纤维和薄膜类微塑料所占比例很小．粒径<1 mm的微塑料数量占总量的49.8%；随着粒径的增大，微塑料数量呈递减趋势(图2(b))．不同类型的微塑料粒径也有差异(图2(c))，碎片类微塑料平均粒径最大，达到2.31±0.58 mm，其次是薄膜(1.82±0.70 mm)和纤维(1.17±0.68 mm)，颗粒类的微塑料最小(0.94±0.56 mm)．由此可见，颗粒类微塑料的丰度在供试土壤样品中占

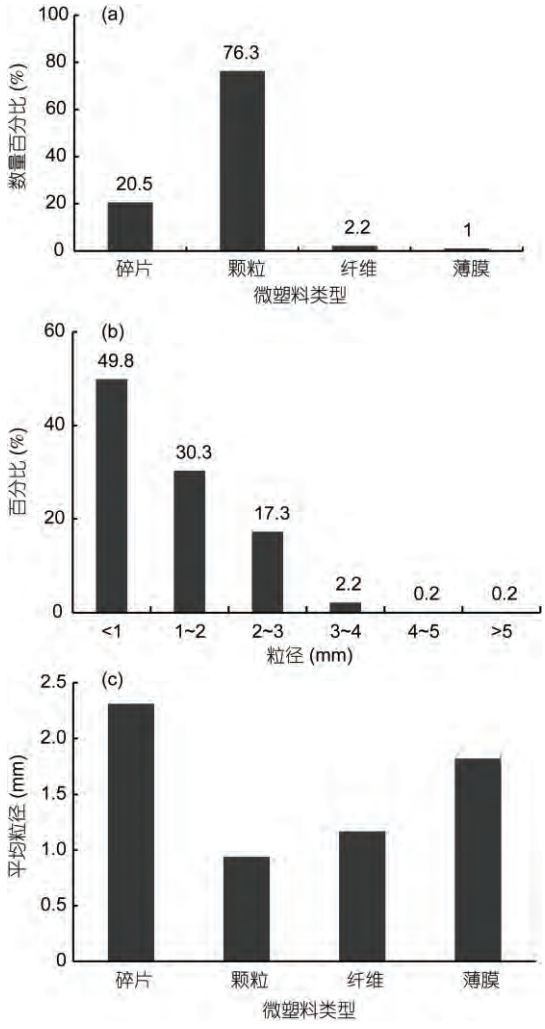

图 2 供试土壤中微塑料类型及其数量百分比(a)、粒径丰度(b)和平均粒径(c)

Figure 2 The percentage of shape types (a), abundance of size fractions (%) (b), and the average size (c) of the different microplastics in the test soil sample

最多的同时，其平均粒径是最小的．这可能与颗粒类微塑料相对较硬、脆化性强等有关，在环境中更易裂解成小颗粒的微塑料[25]．

不同研究区的微塑料丰度有较大差异(表2)．本研究采样区土壤中的微塑料丰度高于新加坡沿海红树林生态系统地区[26]、比利时沿海地区[27]的微塑料丰度．但在粒径和数量关系上与其他调查结果类似，即粒径越小的微塑料，其丰度越大[3,14]．在不同粒径的微塑料中，<1 mm的微塑料已经成为主要的研究对象[27,31~33]．本研究中调查得到的<1 mm的微塑料丰度达50%，与Zhao等人[34]在中国长江入海口水体中观测到的<1 mm的微塑料丰度相当，这些更细小的

表 1　供试土壤样品中提取的微塑料类型、颜色、形状、粒径范围和丰度

Table 1　Color, shape, size range and abundance of microplastics in the test soil sample

类型	颜色	形状	粒径范围(mm)	丰度(*n*/500 g)
碎片	黑色	规则且有破损边缘的扁平形碎片	1.37~4.67	55
	半透明	规则且有破损边缘的扁平形碎片	1.02~3.65	10
颗粒	白色	无固定形状的颗粒	0.12~3.32	242
纤维	蓝色	纤维	0.40~2.63	7
薄膜	透明	无固定形状的薄膜	1.23~2.84	3

表 2　文献中关于调查区土壤或沉积物中微塑料丰度的比较

Table 2　Comparative abundance of microplastics in different study areas as reported in the literature

研究区	微塑料粒径范围	微塑料丰度	来源
新加坡沿海红树林生态系统	<5 mm	3.0±2.0~15.7±6.8 *n*/250 g(干沉积物)	[26]
比利时沿海沙滩	38 μm~1 mm	92.8±37.2 *n*/kg(干沉积物)	[27]
海滩沉积物(大多数)	<5 mm	0.21~77000 n/m^2	[28]
地中海沿海区域(意大利威尼斯潟湖)	<5 mm	2175 *n*/kg(干沉积物)	[29]
加拿大新斯科舍省哈利法克斯港附近	<5 mm	20~80 *n*/10 g(沉积物)	[30]
曹妃甸围填海区潮滩废弃盐场	0.12~4.67 mm	317 *n*/500 g(干沉积物)	本研究

微塑料(1 mm左右或μm级)更容易进入生物体组织甚至细胞中[7,8]，因此未来更需关注丰度较高、颗粒更细的<1 mm的这部分微塑料(MP1). 此外，不同研究区的微塑料类型具有异同性. 与长江口的结果相比，两个地区分离到的纤维、薄膜、颗粒类塑料类型相似，但在形态上仍存在差异. 值得一提的是，本研究区所分离出的黑色碎片类微塑料，至今尚未见文献报道.

2.2　微塑料表面形貌特征

(ⅰ) 微塑料表面整体形貌特征.　供试土壤中微塑料具有复杂的表面形貌，并与其类型有关(图3). 碎片类微塑料沿着两端的风化痕迹较明显，表面有许多沿同一方向的凸起和裂解痕迹. 颗粒类较脆、易粉化，棱角突出、边缘破损程度高. 纤维类微塑料表面凹凸不平，已无成品时的形态. 薄膜类微塑料边缘无固定形状. 同时，同一类型微塑料也会出现形貌差异，如图3(a)和(b)所示的碎片类微塑料，但图3(b)中的微塑料表面比图3(a)的表面具有更明显和复杂的块状突起和撕裂痕迹，几乎遍布于整个表面. 这种差异可能是由于二者风化程度不同所致. Ashton等人[6]通过SEM图像对老化的树脂扁粒表面进行分析并得出与本研究相似的结论，即在这些老化的树脂扁粒表面出现有不同程度的撞击、裂化或粉化的痕迹.

与新购买的同类型商品塑料(图3(f)和(g))相比，上述这些表面形貌特征都是土壤或沉积物环境中微塑料所特有的. 总体来说，土壤环境中的微塑料样品具有表面粗糙、多孔等特点，这种变化会使微塑料形成多孔性表面. 这种多孔表面的形成会使比表面积增大，从而可能增加对污染物吸附的能力[6]. Antunes等人[4]发现老化后的微塑料表面会吸附更多的持久性有机污染物(PCB和DDT)，可能与老化后微塑料表面发生的这些微观形貌变化有关.

(ⅱ) 微塑料表面的孔隙特征.　表面孔隙是微塑料的一个重要表观特征，影响微塑料的表面性质. 如图4所示，这4种微塑料类型都具有不同类型的微孔特征. 有些微孔为纵向撕裂形成(图4(a)和(c))，其微孔长度>50 μm，宽度约为10 μm，微孔中还嵌有纤维状的断裂微塑料残体. 一些均匀裂解形成的微小孔隙(图4(b)和(e))，裂纹方向与裂缝呈90°角，这种一纵一横的裂化使得微塑料表面产生众多块状凸起(其单个凸起的面积大多数不足200 μm^2)，形成的孔隙长度在10~50 μm之间. 有些孔隙是无规则撕裂形成(图4(d)和(f))，孔隙边缘无规则，结构复杂、粗糙且凸凹不平. Corcoran等人[13]认为微塑料表面的纹理特征可用于鉴别微塑料表面的易氧化区，与线性裂纹平行的边缘具有优先氧化的特点.

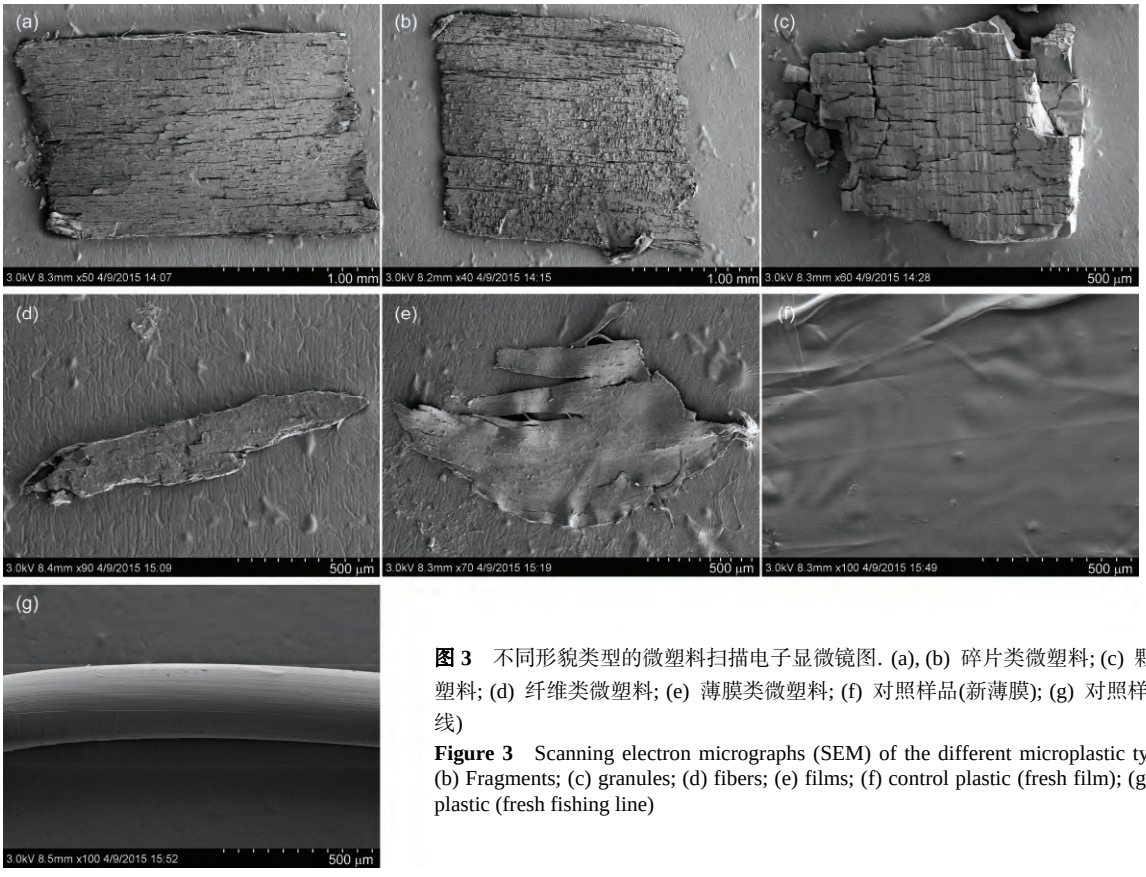

图 3 不同形貌类型的微塑料扫描电子显微镜图. (a), (b) 碎片类微塑料; (c) 颗粒类微塑料; (d) 纤维类微塑料; (e) 薄膜类微塑料; (f) 对照样品(新薄膜); (g) 对照样品(新渔线)

Figure 3 Scanning electron micrographs (SEM) of the different microplastic types. (a), (b) Fragments; (c) granules; (d) fibers; (e) films; (f) control plastic (fresh film); (g) control plastic (fresh fishing line)

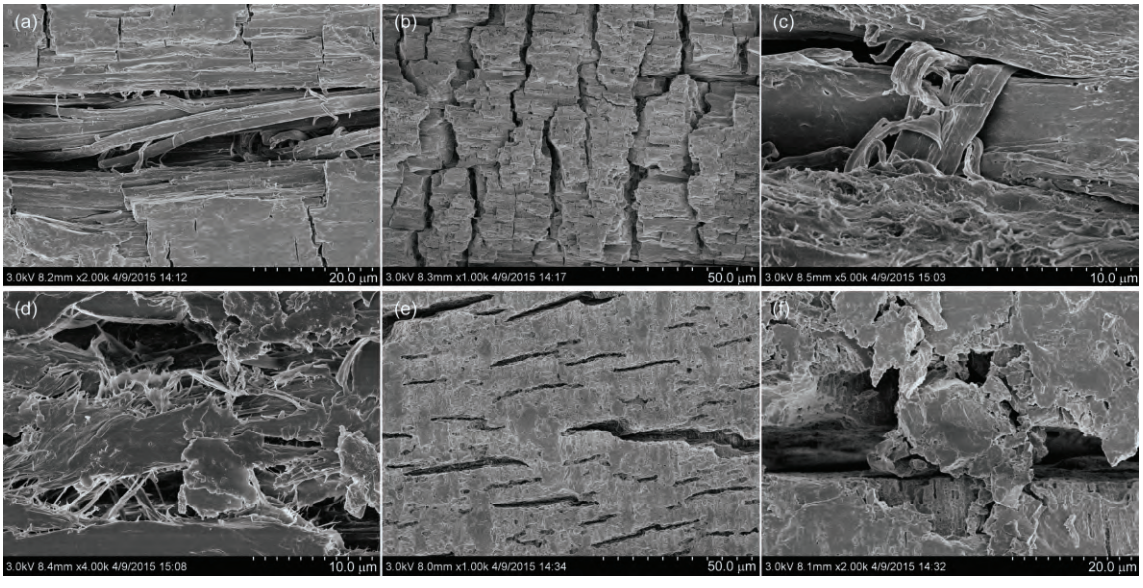

图 4 不同类型微塑料局部表面SEM图. (a), (b) 碎片类微塑料(黑)表面; (c), (d) 碎片类微塑料(半透明)边缘; (e), (f) 颗粒类微塑料孔隙

Figure 4 SEM images of the microscopic features of the microplastics. (a), (b) Surfaces of fragments (black); (c), (d) edges of fragments (semi-transparent); (e), (f) pores of granules

(ⅲ) 微塑料表面的组分特征. 微塑料的多孔表面特性, 会使其表面镶嵌或黏附一些环境物质(如土壤颗粒、有机物质等). 这使微塑料表面变得更为复杂. 本研究通过采用不同的清洗方式, 并结合SEM-

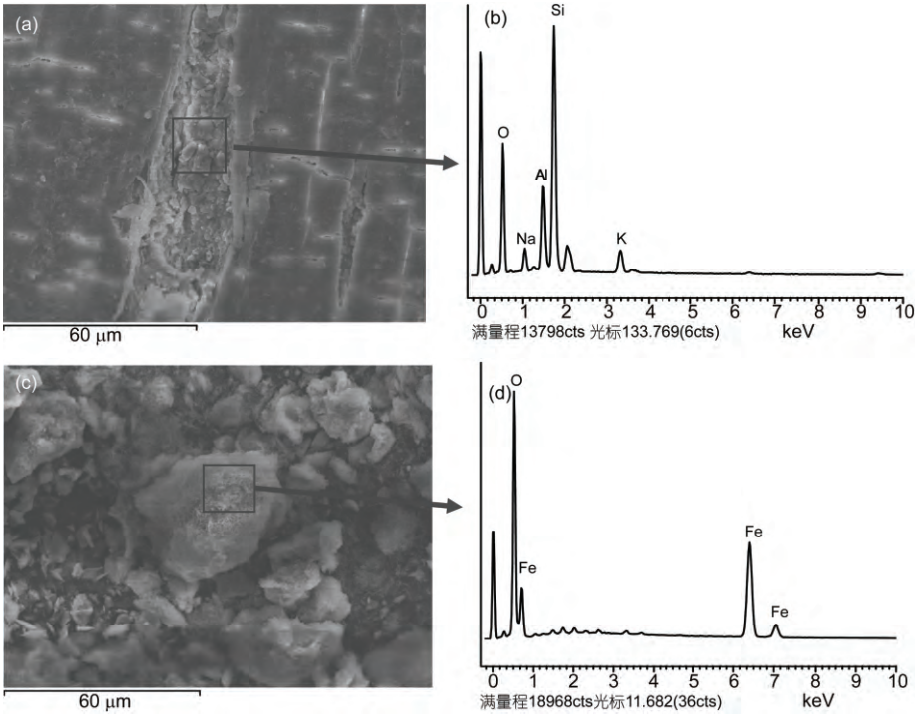

图 5 微塑料表面局部SEM-EDS图. (a), (b) 未超声清洗的碎片类微塑料缝隙杂质及其能谱图; (c), (d) 2 mol/L盐酸超声清洗后的碎片类微塑料表面杂质及其能谱图

Figure 5 SEM images and associated energy spectra of the microplastics. (a), (b) Impurities in silt and the energy spectrum of unwashed fragments; (c), (d) surface impurities and energy spectrum of fragments washed with 2 mol/L HCl solution followed by ultrasonic treatment

EDS分析, 证实微塑料表面确实黏附了一些外来物质. 如图5(a)所示, 微塑料表面的孔隙中存在许多外来杂质, 通过能谱分析发现该杂质为黏土矿物(图5(b)). 这些黏土矿物比较容易被清水冲洗干净. 但有些黏附的物质经盐酸清洗后仍然能够被检测到. 如图5(c)和(d)所示, 经2 mol/L盐酸清洗并超声后, 微塑料表面仍可通过能谱检测到含铁物质(铁氧化物). 铁氧化物在不同的环境条件下会有多种形态存在(如针铁矿、水铁矿、赤铁矿及无定形铁等), 且具有不同的表面特性. 因此, 微塑料表面稳定存在的铁氧化物使得其表面成为一个有机-无机的复合表面, 从而对化学污染物的表面结合状况变得更为复杂, 值得深入研究.

3 结论

研究区曹妃甸潮滩土壤中分离到的4种微塑料类型中黑色碎片类微塑料为首次报道的类型. 粒径<1 mm的微塑料类型丰度最大, 成为主体, 且丰度随着粒径减小而增加. 曹妃甸潮间带土壤环境微塑料样品表面的粗糙纹理、不规则孔隙特征是微塑料的主要表观特征. 表面孔隙在数微米至数十微米之间, 其形态、结构复杂. 微塑料的表面组分特征也较为复杂, 除了在孔隙中镶嵌黏土矿物外, 一些表面还可能存在稳定的铁氧化物, 形成有机-无机复合的表面特征. 因此, 基于微塑料表面特性的污染物结合机制及毒性效应值得深入研究.

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Separation of microplastics from a coastal soil and their surface microscopic features

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Microplastics (<5 mm) are emerging pollutants in the coastal zone and are of worldwide concern. Previous studies have shown the importance of surface features of microplastics on the adsorption and transport of chemical pollutants in the ocean and coastal environment. The objective of this study was therefore to characterize the surface properties of the microplastic samples from a reclamation area polluted by plastic debris in Chaofeidian, Hebei Province. A surface (0–2 cm) soil composite sample was collected from several square plots each with an area of 1 m×1 m. The microplastics were separated in two steps. Firstly, 500 g (dry weight) soil sample was reduced to <100 g soil which contained most of the microplastics using continuous air-flow flotation separation apparatus designed by our own group. Secondly, the microplastics were separated from the soil by density separation using NaI solution (1.8 g cm^{-3}) followed by visual selection. All the microplastics were photographed and image analysis was performed using the program Nano Measurer 1.2 for counting and size measurement. The microscopic features of the microplastic surfaces were characterized using a scanning electron microscope equipped with an energy dispersive spectrometer (SEM-EDS).

Four types of microplastics, namely fragments, granules, fibers and films, were separated from the test soil and black film is a new type of microplastic reported here for the first time. The abundance of all the microplastics was 317 *n* $(500\ g)^{-1}$ (dry weight) at this site with granulate microplastics accounting for 75% of the total abundance followed by fragments accounting for 20%. The size of the microplastics was 1.56±0.63 mm on average and the <1 mm size fraction accounted for 49.8% of the material. The abundance of the different size fractions of the microplastics was negatively correlated with their size in general. Granules were the most abundant type with the smallest average size on the whole. The abundance and size of the microplasitcs found at this site were comparable to those in other study areas such as a coastal sand beach in Belgium and mangrove sediment in Singapore.

The SEM results show weathering features on the microplastic surfaces which were characterized by various porous morphologies and structures. The surface of microplastic samples from the soil was rough with pronounced cavities and similar to previous results observed in coastal environments. However, the surface morphology was distinctly different from that of the virgin plastics. The uneven surface of the microplastics might increase fouling due to changes in surface area and other properties as reported in other studies. We used two solutions (H_2O and 2 mol L^{-1} HCl) to distinguish the foulants between stable and loose combinations. The adhering soil particles were easily removed by washing with water and HCl. However, iron oxides were observed adhering tightly to the surfaces of some of the microplastics and could not be removed by washing with 2 mol L^{-1} HCl. Since there are several types of iron oxides with different surface properties, their stable combination with the mciroplastics might have a pronounced impact on the surface alteration of the microplastics. Moreover, the complicated surfaces of the weathered microplastics likely have very different adsorption characteristics for chemical pollutants compared with the unaltered virgin plastic surfaces. More surface properties of weathered mciroplastics (including pore volume, crystalline structure, and functional groups) must therefore be identified. Moreover, further studies are required to explore the binding mechanisms of chemical pollutants on the microplastic surfaces and the bioaccumulation and ecological toxicity of these combined pollutants with respect to the different surface morphologies and other characteristics of the microplastics with special concern regarding microplastics that are dominated by the <1 mm fraction (MP1).

microplastic pollution, surface micromorphology, abundance, continuous air-flow flotation separation, coastal soil

doi: 10.1360/N972015-01098