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金山湖沉积物微塑料形态与分布特征*

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摘　要　微塑料作为一种新型污染物，对自然环境所造成的潜在风险已成为当前广泛关注的环境问题之一. 湖泊沉积物作为淡水生态系统微塑料的“汇”，其分布特征受所在水域自然及人为等多重因素的影响. 为探究江苏省镇江市金山湖表层沉积物微塑料的分布特征，在 2019 年 1 月（冬季）和 7 月（夏季）选取了 10 个点位采集沉积物样品，并使用金相显微镜观察微塑料样品特征并分类，使用拉曼光谱仪对微塑料聚合物类型进行鉴定，使用扫描电子显微镜分析微塑料表面特征. 结果表明，金山湖冬季和夏季表层沉积物微塑料平均丰度分别为 1368 $n\cdot kg^{-1}$ 和 1112 $n\cdot kg^{-1}$ 干重沉积物，冬季和夏季纤维状微塑料占比分别为 70.5% 和 57.3% 为主，冬季沉积物微塑料颜色所占比例分别为透明（29.50%）、黑色（25.90%）、蓝色（24.10%）、白色（9.71%）、绿色（5.76%）和红色（5.04%），夏季沉积物微塑料各颜色所占比例为蓝色（22.81%）、黑色（21.05%）、绿色（18.13%）、透明（18.13%）、白色（14.33%）和红色（5.56%）. 微塑料以<1 mm 的尺寸在冬季和夏季沉积物中占主导地位，其冬季占比 71.22%，夏季占比 64.62%. 冬季和夏季沉积物中微塑料以聚对苯二甲酸乙二醇酯（polyethylene terephthalate，PET）和聚乙烯（polyethylene，PE）为主要的聚合物类型，冬季 PET 占比为 29.86%、PE 占比为 21.94%，夏季 PET 占比为 33.04%、PE 占比为 22.81%. 在冬季和夏季沉积物微塑料表面均存在粗糙、撕裂、多孔等情况.

关键词　季节，沉积物，微塑料，湖泊.

Morphology and distribution characterization of microplastic in sediments of Jinshan Lake

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Abstract　Microplastics (MPs), as a new type of environmental pollutant, has received widespread attention owing to their potential risks to the natural environment. Sediments are the "sinks" for MPs in freshwater lake ecosystems and the distribution characteristics of MPs were affected by multiple factors of natural and human. In this paper, total 10 sampling sites from the Jinshan lake of Zhenjiang city were selected and surface sediments were sampled both January (winter) and July (summer) of 2019, respectively. In addition, MPs in sediment samples were classified using metallographic microscopy, and their microplastic polymer and surface characteristics were identified and analyzed

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using Raman spectroscopy and scanning electron microscopy, respectively, in order to determine the morphology and distribution characterization of MPs in sediments of Jinshan Lake. Results showed that the average abundance of microplastics was 1368 $n\cdot kg^{-1}$ in the winter and 1112 $n\cdot kg^{-1}$ in the summer. Fibrous microplastics were the predominant MPs, which accounted for the higher proportion of 70.5% and 57.3% in winter and summer, respectively. In addition, the colors of microplastics in winter sediments were transparent (29.50%), black (25.90%), blue (24.10%), white (9.71%), green (5.76%) and red (5.04%), respectively. The proportion of microplastics colors in summer sediments were blue (22.81%), black (21.05%), green (18.13%), transparent (18.13%), white (14.33%) and red (5.56%). Small-sized particles (<1 mm) were the predominant size, with the percentage of 71.22% and 64.62% in winter and summer respectively. Polyethylene terephthalate (PET) and polyethylene (PE) were the two main polymer types in this study. PET and PE accounted for 29.86% and 21.94% in winter, whereas, PET accounted for 33.04% and PE accounted for 22.81% in summer. The surface of microplastics in both seasons was rough, torn and porous.

Keywords season, sediment, microplastic, lake.

近年来,塑料制品生产及使用量急剧增加,加之塑料垃圾处理不当和回收率低的原因,导致塑料在自然环境中大量积累[1]. 据报道至 2050 年,全球每年塑料产量可能达到 330 亿吨[2]. 数量巨大的塑料制品在光照、海浪冲击、侵蚀、风化等外界作用下会逐渐分解为直径小于 5 mm 的小塑料颗粒,即微塑料. 微塑料在环境中具有持久性且不易降解的特点[3],其长时间暴露在环境中[4]易造成潜在的环境风险[5-6]. 作为一种新型污染物,微塑料所引发的生态安全已成为全球关注的热点环境问题之一[7].

目前,微塑料已在水生态系统中被广泛检出[8]. 如中国南海、渤海、东海等海域[9-10],黄河、长江等河流[11-12],鄱阳湖、南湖等湖泊均发现不同程度的微塑料污染[13-14]. 已有研究表明,沉积物是淡水生态系统微塑料的"汇"[15]. 沉积物中微塑料的累积、迁移和分布受气象条件、水流和水生生物等在内的多种因素的影响[16-18]. 此外,微塑料的数量也与人口和人类活动(如船舶、港口作业、捕鱼、塑料生产和污水处理)密切相关[19-20]. 可见,沉积物微塑料的分布与所在水域自然及人为因素的影响密不可分,针对特定水域开展湖泊沉积物中微塑料分布特征的调查,将对该水域微塑料污染背景数据的积累具有重要意义.

本研究以金山湖沉积物为研究对象,研究金山湖沉积物微塑料的丰度、分布特征和季节变化规律,评估微塑料在金山湖沉积物中的污染情况,研究结果将为半封闭式闸坝型城市湖泊沉积物中微塑料的污染状况提供基础数据.

1 材料与方法(Materials and methods)

1.1 研究区概况

研究区域位于江苏省镇江市金山湖,该区域属于亚热带湿润气候,平均气温 14.8—15.3 ℃,平均年降水量为 1044.6 mm[21].

金山湖(32°13'4.652"—32°14'35.79"N ,119°25'5.711"—119°29'48.049"E)位于江苏省镇江市内,金山湖东西方向长约 4 km,南北宽约 2 km,湖泊丰水期面积为 8.8 km^2,在镇江城市地表水中所占面积约 80% 以上[22],是镇江市最大的景观湖泊和重要的防洪水体,且是镇江市金山、焦山、北固山"三山"名胜景区的核心所在[23]. 该湖泊为闸坝型水体,1987 年来开通了连接金山湖与长江的引航道[24],引航道闸坝从长江引水进入金山湖,并穿过下游胶南坝使水回流至长江,从而实现金山湖水位的调控[25].

1.2 样品采集及预处理

在综合考虑镇江市金山湖水体分布特征、水域面积及人类活动的程度等基础上,在金山湖共选取 10 个点位进行样品采集,具体点位见图 1 所示.

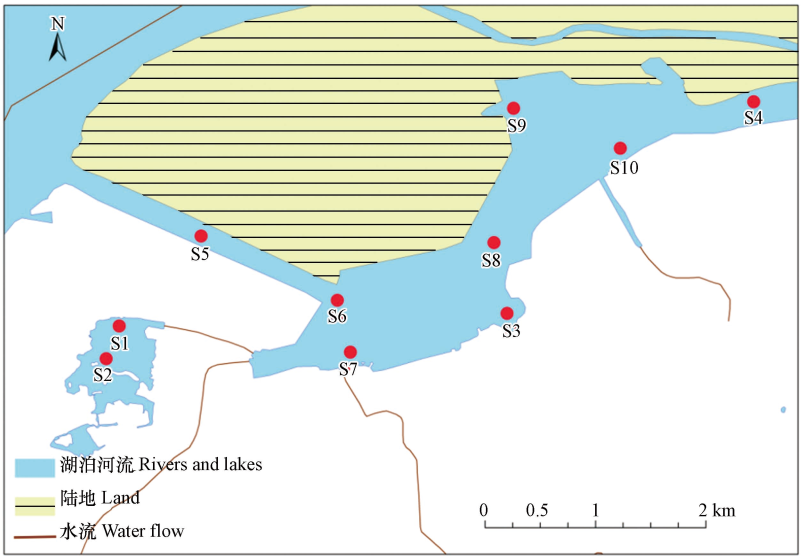

图 1　金山湖采样点位

Fig.1　Sampling sites of Jinshan Lake

采用彼德森抓泥斗抓取沉积物, 在 2019 年 1 月(冬季)和 7 月(夏季)在选取的 10 个点位采集表层沉积物样品, 每个点位采集 3 个平行样, 将同一采点位样品充分混匀, 带回实验室. 将样品在 45 ℃ 的烘箱中烘干、砸碎、过 5 mm 筛, 并用铝箔包好, 保存在干燥处储存, 用于微塑料的样品前处理.

1.3　微塑料提取

采用密度分离法提取沉积物中微塑料[26]. 首先将 50 g 沉积物样品(干重)转移到一个干净的锥形瓶中, 加入 500 mL 饱和氯化钠溶液, 用干净的玻璃棒搅拌 2 min, 直到沉积物和溶液完全混匀. 瓶子用铝箔密封, 以防止样品污染, 并静置 24 h, 等待固体和液体分离完全, 确保微塑料完全悬浮在上清液中. 随后, 将上清液转移到另一个干净的锥形瓶中, 并在剩余的沉积物中加入饱和碘化钠溶液, 进行二次浮选. 重复上述相同的步骤来分离固体和液体. 为避免有机质的干扰, 在提取的上清液总加入 30% 的过氧化氢溶液, 然后用铝箔将瓶子密封, 在 45 ℃ 的水浴中加热 48 h. 待有机质消解后, 使用 Φ50 mm×0.45 μm 醋酸纤维素膜对上清液进行真空过滤, 将滤膜置于培养皿中保存, 以备后续对微塑料的观测.

1.4　微塑料的鉴别

采用金相显微镜(CX40M, Ningbo Sunny, China)在放大 50—100 倍下通过软件 IMSA-2000 对干燥滤膜上的微塑料进行拍照计数. 研究表明[27], 微塑料按形态特征分为即纤维、颗粒、碎片、薄膜状微塑料共 4 种类型. 按颜色分为红色、蓝色、绿色、透明、白色和黑色共 6 类[28]. 根据其粒径不同可分为 <0.5、0.5—1、1—2、2—3、3—4、4—5 mm 等类型[28－29].

选择具有代表性的微塑料样品, 采用拉曼光谱仪(DXR, Thermo Fisher, USA), 根据已知的聚合物光谱确定微塑料的聚合物类型, 对微塑料样品的化学组成进行识别[30]. 由于样本量较大, 采用所有颜色及形状的微塑料组合, 以确保所有类型都被检测到, 并且根据显微镜的观察进行微塑料聚合物类型的统计分析.

本研究中, 利用扫描电子显微镜结合能量光谱仪(SEM/EDS), 研究了微塑料样品的表面性质. 即: 用拉曼分析对微塑料进行鉴定后, 将样品涂上铂薄膜, 用 20 kV 扫描电镜(S-3400N, Hitachi, Japan)与可变真空钨丝观察. 由于微塑料表面的侵蚀程度不同, 在不同的表面位置和粗糙度下至少进行了 3 次可视化分析.

1.5　数据计算与分析

使用软件 WPS Office 进行数据的处理和表格的绘制. 本研究采用双因素方差分析来确定在 P<为 0.05 时, 微塑料的季节变化和空间变化是否具有统计学意义. 采用 SPSS v. 27(IBM 公司, Armonk, NY, USA)进行空间与季节的双因素方差分析. 微塑料丰度数值采用平均值表示, 丰度采用每 kg 干重沉积物的颗粒数表示, 单位为 n·kg^{-1} .

2 结果与讨论(Results and discussion)

2.1 微塑料的季节与空间分布

由图 2 可知,金山湖所有点位表层沉积物均检测到了微塑料,夏季沉积物中微塑料丰度范围为 720—2440 n·kg^{-1} 干重沉积物,平均丰度为 1368 n·kg^{-1},冬季则为 600 — 2280 n·kg^{-1},平均丰度为 1112 n·kg^{-1} 干重沉积物. 对比其他湖泊沉积物微塑料丰度值后发现,金山湖微塑料丰度低于牛轭湖沉积物(347—4031 n·kg^{-1} 和 507—7593 n·kg^{-1})[31],高于太湖沉积物微塑料丰度(11.0—234.6 n·kg^{-1})[32]、雨山湖(278.9、277.1 n·kg^{-1})[33] 和洞庭湖(180—693 n·kg^{-1})[34]. 金山湖沉积物微塑料丰度平均值与鄱阳湖相近(921.6 n·kg^{-1} 和 996.2 n·kg^{-1})[15]. 总体而言,本研究所测金山湖沉积物微塑料丰度值在中国已观测的沉积物微塑料丰度范围之内.

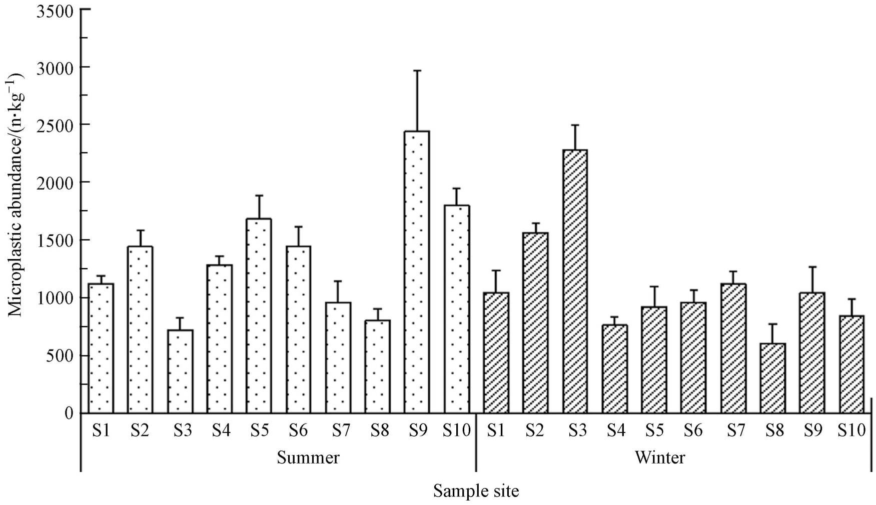

图 2 金山湖流域冬夏季的微塑料丰度

Fig.2 Winter and summer microplastics abundance in Jinshan Lake basin

金山湖沉积物微塑料丰度值冬季两季变化明显. 冬夏两季 10 个采样点沉积物微塑料丰度值的方差分析结果表明,S3、S4、S5、S6、S9 和 S10 点位在两个季节丰度值存在显著差异($P<0.05$). 其中,S2、S3 和 S7 采样点沉积物微塑料丰度平均值表现为冬季>夏季,其余点位则表现为夏季>冬季,由此可判断,金山湖 70% 沉积物在夏季微塑料丰度略高于冬季,这与夏季降雨量较大等有一定的关系. 研究表明,降雨充沛时微塑料可从陆地转移到湖泊沉积物,从而使湖泊沉积物中微塑料丰度升高[35].

除了季节差异,沉积物中微塑料丰度在空间分布上亦表现出显著的差异($P<0.01$). 已有研究表明,河流和湖泊等环境中微塑料丰度与人类活动等因素密切相关[36-37]. 人类活动较为频繁的地区往往会造成严重的塑料堆积和污染[19]. 如研究发现人流量增加引起微塑料的丰度显著升高[38-39]. 而城市较高的人口密度引起的塑料制品消费增加也会产生更多的微塑料污染[40]. 金山湖位于镇江市中心,作为镇江市的著名风景区吸引大量游客,尤其是夏季,大量的游客在金山湖水域开展各项活动,增加了塑料制品的污染风险. 其次,城市建筑材料、汽车轮胎等频繁使用,将导致微塑料随大气干、湿沉降以及随地表径流等从陆地进入湖泊生态系统[41].

2.2 微塑料的形态分布特征

金山湖表层沉积物微塑料从形态上主要分为 4 类: 纤维状、颗粒状、碎片状和薄膜状(图 3). 夏季沉积物微塑料中,纤维状微塑料占比 57.3%,其次是碎片状(26.3%)、颗粒状(11.1%)和薄膜状(5.3%); 冬季沉积物微塑料中,纤维状微塑料占比 70.5%,其次是碎片状(16.2%)、颗粒状(7.9%)和薄膜状(5.4%). 冬夏两季微塑料形状占比均表现为: 纤维状>碎片状>颗粒状>薄膜状,表明冬夏两个季节金山湖沉积物中微塑料形态组成均以纤维状为主,这与 Malla-Pradhan 等[42] 在费瓦湖沉积物的研究结果类似. 已有研究表明,纤维状微塑料具有大的比表面积,因此生物膜易附着在其表面,可降低纤维状微塑料的浮力[43],促使其沉降. 此外,纤维状微塑料还可能与渔业和生活污水排放有关. 研究表明[44],洗衣机

出水中纤维状微塑料丰度可达 100 n·L^{-1}; 其次, 老化的渔网渔具也会形成纤维状的微塑料[45]. 除了纤维状微塑料, 其他形态如碎片状和薄膜状等主要是塑料制品自然分解所产生, 如塑料包装袋、农用地膜和塑料容器[46]. 颗粒状微塑料主要来源于个人护理及化妆品等, 如调查发现面部擦洗产品中微塑料平均含量约为 20.86 n·mg^{-1}[47].

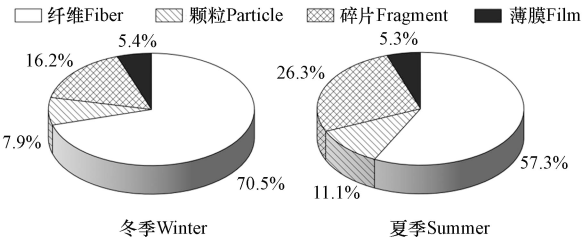

图 3 金山湖不同季节水体中微塑料的形状占比

Fig.3 Percentage of microplastics shape in water bodies in different seasons in Jinshan Lake

2.3 微塑料的颜色和粒径分布特征

金山湖沉积物中共检出 6 种颜色微塑料, 其中红色、蓝色、绿色归类为彩色微塑料. 如图 4(a)夏季沉积物微塑料颜色占比分别为蓝色(22.81%)>黑色(21.05%)>绿色(18.13%)=透明(18.13%)>白色(14.33%)>红色(5.56%); 冬季沉积物微塑料颜色则表现为透明(29.50%)>黑色(25.90%)>蓝色(24.10%)>白色(9.71%)>绿色(5.76%)>红色(5.04%). 夏季蓝色微塑料占优势, 而冬季透明微塑料占比最高, 此外, 夏季彩色微塑料显著高于冬季的彩色微塑料, 如绿色微塑料可能来源于渔网、渔具等. 此外, 目前市场上彩色塑料制品占比较高也是沉积物彩色微塑料丰度较高的重要原因之一[48]. 黑色微塑料可能是农用地膜和轮胎使用所产生. 已有研究表明, 在光照的作用下环境中微塑料易发生风化, 含氧官能团的增加导致微塑料发生褪色[49]. 基于多种因素, 金山湖沉积物微塑料颜色呈现出多样性的特征. 而彩色微塑料与营养水平较低的生物体类似, 更易被生物摄食[50], 从而增加了生态风险.

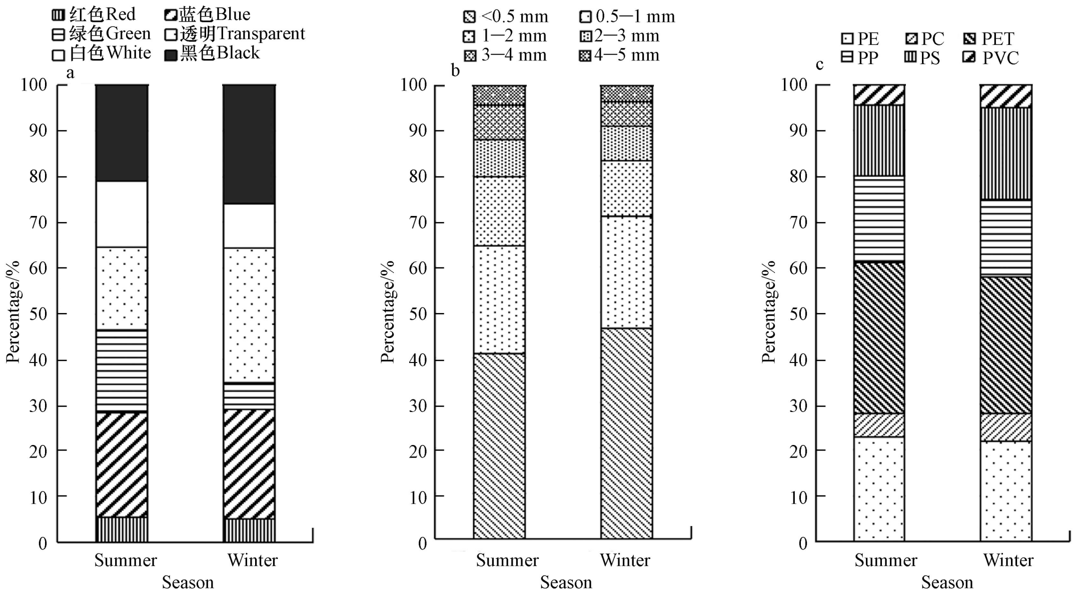

图 4 夏季和冬季金山湖表面沉积物微塑料的相对占比

(a)颜色(b)粒径(c)聚合物类型

Fig.4 Relative proportion of microplastics in summer and winter sediment sediments on the surface of Jinshan Lake

(a) color (b) particle size (c) polymer type

微塑料按其粒径可分为<0.5、0.5—1、1—2、2—3、3—4、4—5 mm 共 6 个范围[51]. 如图 4(b)所示, 金山湖沉积物冬夏两季微塑料丰度均随粒径的增加而减小, 这与洞庭湖[52], 三峡水库[53] 等研究结果一致. <0.5 mm 微塑料的丰度最高, 冬夏季分别占微塑料总量的 46.40% 和 40.94%, 这与其他研究结果类似, 如鄱阳湖沉积物中<0.5 mm 粒径的微塑料>70%[54], 雨山湖和南湖沉积物粒径<0.5 mm 的微塑料分别占比 46.02% 和 62.79% 的[33].

此外,将<1 mm 的微塑料定义为较小尺寸的微塑料[55],按此标准,冬季<1 mm(71.22%)的微塑料占比略高于夏季(64.62%),表明在两个季节中较小尺寸微塑料占主要优势,这可能与金山湖的水位调控,以及长江支流等[56] 水体中<1 mm 的微塑料占主要优势有关. 研究已证实,小尺寸微塑料占比高的原因可能由于污水处理厂不能对小尺寸微塑料进行很好的去除[57];此外,小尺寸的微塑料可能是大尺寸的塑料经过机械磨损、氧化和生物等作用下发生碎裂和降解所形成[58]. 由于小尺寸微塑料具有较大的比表面积,能对环境中的重金属离子等有害元素进行吸附,往往成为这些有害元素的载体,极易被水生生物摄食并在食物链中循环,从而产生生物毒性效应[59−60],并最终对人类健康造成危害. 由于较小尺寸的微塑料粒径小,沉积物中的较小尺寸微塑料更容易二次悬浮至水中,加剧水体危害[61]. 因此,沉积物中较小尺寸的微塑料在湖泊生态系统中具有更大的潜在生态风险.

2.4 微塑料的聚合物类型及其表面形貌

利用拉曼光谱仪对微塑料成分进行检测后发现,金山湖沉积物微塑料共有 6 种聚合物类型,分别为聚乙烯(polyethylene PE)、聚碳酸酯(polycarbonate PC)、聚对苯二甲酸乙二醇酯(polyethylene terephthalate PET)、聚丙烯(polypropylene PP)、聚苯乙烯(polystyrene PS)和聚氯乙烯(polyvinyl chloride PVC). 金山湖冬夏两季沉积物微塑料聚合物类型较为相似,冬季沉积物中 PET 占优势(29.86%),其次为 PE(21.94%)、PS(20.14%)、PP(16.91%)、PC(6.12%)和 PVC(5.04%),夏季沉积物 PET、PE、PP、PS、PC、PVC 占比分别为 33.04%、22.81%、19.01%、15.50%、5.26% 和 4.39%,占比最少的为 PC 和 PVC. 以上微塑料都是较为常见的聚合物类型. 其中,PE 主要用于农用地膜、网和钓鱼线等;PC 主要来源于建筑材料、汽车和其他工业用途,PET 是纺织品常见的组成部分,其可以通过洗涤废水进入湖泊中,这可能是湖泊沉积物 PET 微塑料占比较高的主要原因;PP 是服装、医疗等生活必须品的主要原材料;PS 和 PVC 则通常用于包装和工业目的[62]. 由此可推测金山湖沉积物中微塑料污染可能主要来源于洗涤废水、包装和老旧渔具等,在今后的研究中需进一步追溯其源头. 扫描电镜的结果显示金山湖沉积物中的微塑料均呈现表面粗糙、多孔、撕裂和裂缝,表明由于水流及沉积物的运动,微塑料经历了不同程度的侵蚀和风化(图 5).

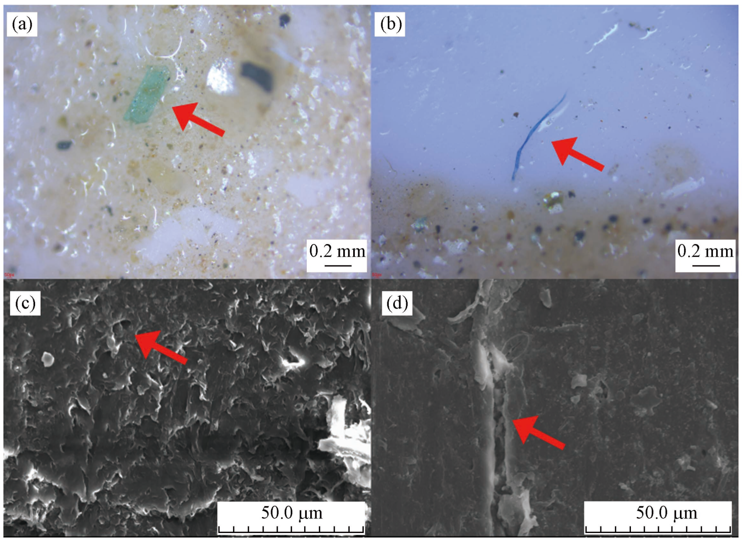

图 5 沉积物中微塑料物理形貌特征

(a、b)绿色碎片、蓝色纤维微塑料显微照片; (c、d)多孔、撕裂微塑料扫描电镜照片

Fig.5 Physical topography of microplastics in sediments

(a, b) green fragment,blue fiber microplastic micrographs; (c, d) porous,torn microplastic scanning electron microscopy photos

3 结论(Conclusion)

(1)金山湖沉积物中微塑料夏冬季平均丰度分别为 1368 n·kg^{-1} 和 1112 n·kg^{-1},夏季表面沉积物中微塑料丰度平均值高于冬季.

(2)金山湖沉积物中微塑料的形状包括纤维状、碎片状、颗粒状和薄膜状, 其中纤维状微塑料在夏季和冬季沉积物中均占比最高, 分别为 57.3% 和 70.5%.

(3)金山湖冬季沉积物中微塑料颜色分别为透明(29.50%)、黑色(25.90%)、蓝色(24.10%)、白色(9.71%)、绿色(5.76%)和红色(5.04%); 夏季沉积物微塑料颜色分别为蓝色(22.81%)、黑色(21.05%)、绿色(18.13%)、透明(18.13%)、白色(14.33%)和红色(5.56%).

(4)金山湖冬季和夏季沉积物中微塑料以较小尺寸(<1 mm)微塑料为主, 占比分别为 71.22% 和 64.62%.

(5)冬季和夏季金山湖沉积物中微塑料聚合物类型均以 PET 和 PE 为主, 冬季沉积物中 PET 和 PE 分别占总数的 29.86% 和 21.94%; 夏季沉积物微塑料 PET 和 PE 分别占总数的 33.04% 和 22.81%.

(6)冬夏两季金山湖沉积物中微塑料均存在表面粗糙、多孔、撕裂和裂缝等情况.

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