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微塑料对土壤中养分和镉淋失的影响

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摘要: 微塑料作为新兴污染物, 具有尺寸小、比表面积大、吸附能力强和降解慢等特点, 其环境效应受到越来越多的关注. 微塑料会改变土壤性质, 影响土壤中养分和污染物的迁移能力, 但是微塑料对土壤养分和重金属淋失的影响尚缺乏研究. 通过土壤柱浸滤实验比较研究了在模拟降雨条件下不同质量分数(0%、0.2%和2%)的聚苯乙烯(PS)和聚乳酸(PLA)微塑料对土壤中养分和镉淋失的影响. 总体上, 降雨强度增加会促进土壤中养分和镉的淋失. 2% PS在大暴雨时显著增加总氮的淋失和土壤中有效磷含量, 减少了无机磷的淋失和土壤铵态氮含量, 大雨时增加土壤速效钾含量. 大雨和暴雨时 2% PLA 减少了硝态氮的淋失, 暴雨和大暴雨时降低土壤铵态氮含量, 大暴雨时降低土壤总氮的含量, 且大暴雨时 0.2% PLA 显著增加镉的淋失. 结果显示, 微塑料对土壤养分和镉淋失的影响与微塑料的种类和质量分数有关, 并受到降雨水平的影响. 研究表明, 难降解微塑料聚苯乙烯和可降解微塑料聚乳酸都会对土壤中养分和重金属的淋失产生影响.

关键词: 微塑料(MP); 重金属; 养分淋失; 硝态氮; 镉(Cd)

中图分类号: X131.3 文献标识码: A 文章编号: 0250-3301(2024)01-0489-07 DOI: 10.13227/j.hjxx.202302097

Effects of Microplastics on the Leaching of Nutrients and Cadmium from Soil

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Abstract: The environmental effects of microplastics, which are considered a type of emerging contaminants, have attracted increasing concern due to their small size, large specific surface area, strong adsorption capacity, and low degradability. Microplastics can change soil properties and affect the migration ability of nutrients and pollutants in soil, but their effects on the leaching of soil nutrients and heavy metals have not been sufficiently studied. A soil column leaching experiment was conducted to explore the effects of polystyrene (PS) and polylactic acid (PLA) microplastics at different mass fractions (0%, 0.2%, and 2%) on the leaching of nutrients and cadmium under simulated rainfall scenarios. The results showed that increasing rainfall intensity enhanced the leaching of nutrients and cadmium from soil. During downpour conditions, 2% PS significantly increased the leaching of total nitrogen and the content of available phosphorus in soil and reduced the leaching of inorganic phosphorus and the content of ammonium nitrogen in the soil, whereas it increased the content of available potassium during heavy rain. By comparison, 2% PLA reduced the leaching of nitrate nitrogen during heavy rain and intense rainfall and decreased the content of ammonium nitrogen in soil during intense rainfall and downpour conditions and the content of total nitrogen in soil during downpours. In addition, 0.2% PLA significantly increased cadmium leaching during downpours. To conclude, the effects of microplastics on the leaching of nutrients and cadmium were dependent on the type and concentration of microplastics, as well as the rainfall level. Our findings showed that the microplastics derived from both nondegradable PS and biodegradable PLA could affect the leaching of nutrients and heavy metals from soil.

Key words: microplastics(MP); heavy metals; nutrient leaching; nitrate nitrogen; cadmium (Cd)

随着塑料制品的广泛使用, 微塑料(尺寸 < 5 mm)在生态系统中的分布和效应受到越来越多的关注. 微塑料来源众多, 例如农膜使用、污泥堆积、日常生活排放和大气沉降等^[1]. 土壤环境是最终的汇源地之一^[2], 因此土壤生态系统中的微塑料受到重视^[3]. 微塑料不仅对土壤环境中的动植物以及微生物产生直接影响, 也可以通过改变土壤理化性质产生间接影响^[4-6]. 微塑料也会通过吸附作用、改变土壤性质等多种途径直接或间接影响养分和重金属的形态和迁移^[6-8]. 微塑料也可以通过食物链进入人体危害人体健康^[4,9].

微塑料会直接吸附重金属^[10]、有机污染物^[11]和土壤养分^[12]等. 微塑料自身性质和环境因素的不同造成了微塑料在土壤中吸附行为的复杂性^[7,13]. 微塑料在土壤中的吸附与土壤的 pH、团聚体和容重等有关^[14], 还与微塑料的种类、粒径、形状和表面特性等

相关^[7,15]. 微塑料在土壤中会通过生物和非生物因素在土壤中迁移^[16], 可能会通过载体效应影响土壤养分和污染物的迁移^[17].

镉(Cd)是土壤中常见的有毒重金属, 其溶解度较高, 容易在土壤环境中迁移^[18], 也容易被植物吸收进入食物链. 降雨会使得土壤中的养分和镉发生淋失, 通过地表径流引起地表水富营养化^[19]和镉污染, 向下淋溶迁移会引起地下水污染. 微塑料与重金属都是常见的土壤污染物, 目前有研究表明微塑料会影响土壤中养分和重金属的移动性和有效性^[6], 但是在模拟降雨条件下微塑料对土壤养分和重金属的淋失的影响尚缺乏研究. 本研究通过探究不同降雨情

收稿日期: 2023-02-14; 修订日期: 2023-03-24

基金项目: 山东省自然科学基金项目(ZR2020MD120)

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况下微塑料对土壤中养分和镉淋失的影响,旨在为了解微塑料的环境风险提供参考。

1 材料与方 法

1.1 供试材料

供试土壤为非农业土壤,近两年未耕种。取自山东省青岛市南泉镇。土壤在经过室温风干后过 2 mm 筛备用。土壤 pH 为 5.63, ω (有机质)为 $11.8 \text{ g}\cdot\text{kg}^{-1}$, ω (铵态氮)为 $1.7 \text{ mg}\cdot\text{kg}^{-1}$, ω (硝态氮)为 $40.2 \text{ mg}\cdot\text{kg}^{-1}$, ω (有效磷)为 $9.8 \text{ mg}\cdot\text{kg}^{-1}$, ω (速效钾)为 $53.6 \text{ mg}\cdot\text{kg}^{-1}$ 。

供试塑料为目前广泛应用的传统难降解塑料聚苯乙烯(PS)和可生物降解塑料聚乳酸(PLA),使用前过 200~400 目筛子,使微塑料的粒径在 0.075 mm 和 0.038 mm 之间。装土壤的塑料柱高为 20 cm(模拟土壤耕作层深度),外径 8.2 cm,内径 8.0 cm,柱内表面积为 50.2 cm^2 ,柱内壁用砂纸打磨后用蒸馏水清洗干净。

1.2 浸滤实验设计

土壤柱实验参考前人设计^[20]。实验设计和土壤浸滤实验设计了三因素实验,包括 2 种微塑料、3 个微塑料质量分数(0、0.2% 和 2%)和 3 种不同的降雨强度(大雨 200 mL,暴雨 400 mL,大暴雨 600 mL)。每个处理设置 3 个重复,共计 15 个处理。CK 表示未添加微塑料的土壤,为对照组,0.2% PLA 和 2% PLA 表示土壤中添加了 0.2% 和 2% 的 PLA,0.2% PS 和 2% PS 表示土壤中添加了 0.2% 和 2% 的 PS。降雨量根据中国气象局降雨等级划分^[21]。微塑料含量参考已有报道的土壤微塑料丰度^[22]。 $\omega(\text{Cd})$ 为 $5 \text{ mg}\cdot\text{kg}^{-1}$ 代表了部分中国土壤环境现实的 Cd 污染状况^[23]。将氯化镉溶液喷洒到土壤并充分搅拌后放置到黑暗处,平衡 2 周后晾干,然后按照目标剂量将微塑料均匀混入到 Cd 污染土壤中。随后将土壤装在柱里,将土壤表面抹平,模拟田间土壤。然后灌注一定量的蒸馏水,使得土壤含水量达到野外取样时的土壤含水量(23% 左右)。将土壤静置,使土壤中的水分能够均匀分布。静置期间每 3 d 浇一次水,用称重法补充水量。30 d 后对土壤柱进行浸滤实验,每 2 周浸滤一次,共 4 次。浸滤结束以后取部分新鲜土样品冷藏保存,再取部分土样风干备用。

1.3 测定指标和方法

浸滤液收集后测定其体积,经 $2.2 \mu\text{m}$ 的膜过滤后取 100 mL 用于测定养分和镉含量。测定方法均参考《水和废水监测分析方法(第四版)》^[24]。硝态氮采用紫外分光光度法,氨氮采用纳氏试剂法,总氮采用过硫酸钾氧化-分光光度法,总钾和镉含量

采用原子吸收法测定。土壤铵态氮和硝态氮采用氯化钾溶液提取-分光光度法^[25]测定。土壤总氮采用自动定氮仪法^[26]测定,土壤速效钾采用乙酸铵浸提法^[27]测定。

1.4 数据分析

数据采用 IBM SPSS Statistics 19 进行统计分析,对照和处理之间采用单因素方差分析(ANOVA)法处理分析(邓肯检验),设定 $P < 0.05$ 为显著水平,三因素方差分析检测雨量、微塑料种类和质量分数的主效应和交互作用。使用 Origin 2018 进行绘图。

2 结果与分析

2.1 浸滤液和土壤硝态氮

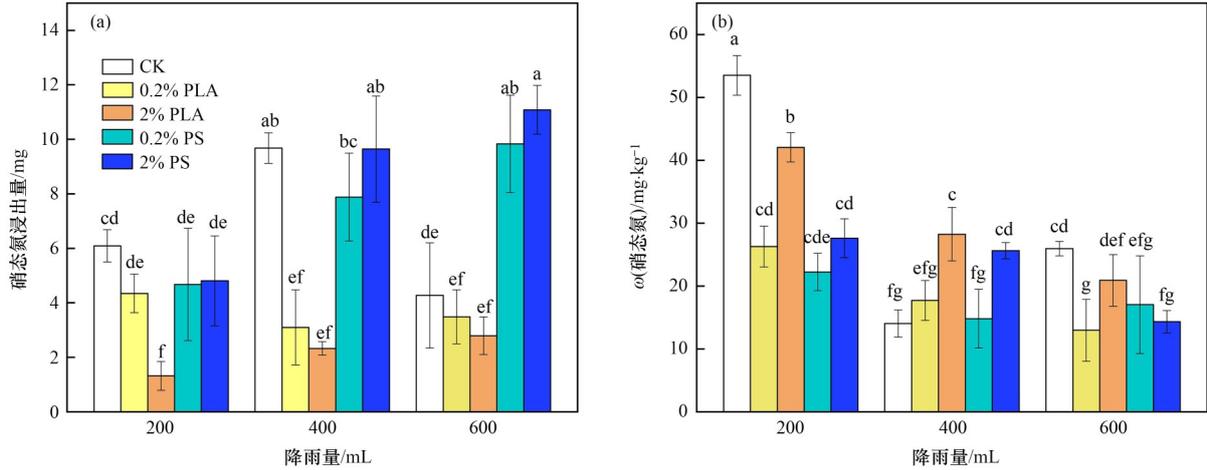
图 1 中养分浸出量为 4 次浸滤液中的养分总量。除大暴雨量外,其他降雨量时微塑料都会减少土壤中硝态氮的淋失,其中大雨量时 2% PLA 处理比对照显著减少了 78.35% [图 1(a)]。暴雨量时,2% PLA 和降幅 0.2% PLA 处理都显著减少了土壤中硝态氮的淋失,降幅分别是 75.96% 和 68.01%。微塑料种类、降雨量以及二者的交互作用对硝态氮的淋失具有显著影响(表 1)。大雨量时 2% PLA 和 0.2% PLA 处理显著减少了土壤中硝态氮的含量 [图 1(b)],降幅分别是 50.89% 和 21.39%。三因素方差分析(表 1)显示,微塑料质量分数和降雨量、微塑料种类和降雨量对土壤硝态氮含量有显著交互作用。

2.2 浸滤液氨氮和土壤铵态氮

降雨量显著影响土壤中氨氮的淋失,浸滤液中的氨氮随降雨量增加而增加 [图 2(a)]。各微塑料处理之间没有显著差异。三因素方差分析结果发现,只有降雨量对浸滤液中氨氮含量有显著影响(表 1)。大雨量时 0.2% PS 处理的土壤铵态氮含量比对照高 43.62% [图 2(b)]。暴雨时,2% PLA 处理中铵态氮的含量比对照显著降低 18.23%。大暴雨时,0.2% PLA 处理比 2% PLA 显著增加 18.24%。三因素方差分析(表 1)显示微塑料种类、质量分数以及降雨量对土壤铵态氮含量存在显著交互影响。

2.3 浸滤液和土壤总氮

如图 3(a)所示,大雨量和暴雨量时,高质量分数和低质量分数的 PLA 都显著减少了土壤中总氮的淋失。大雨量 2% PLA 和 0.2% PLA 处理比对照显著减少了 57.16% 和 48.48%,暴雨量时 2% PLA 和 0.2% PLA 处理分别比对照减少 62.77% 和 55.74%,大暴雨量时 2% PS 处理的总氮淋失量最高,比对照显著高 54.50%。根据三因素方差分析(表 1),降雨量与微塑料种类、质量分数之间对浸滤液中总氮存在有显著交互作用。暴雨量时,高质量分数微塑料土壤的总氮



不同小写字母表示差异显著($P < 0.05$),下同

图1 不同微塑料和降雨水平下硝态氮浸出量和土壤中硝态氮含量

Fig. 1 Amount of nitrate nitrogen in leachate and nitrate nitrogen content in soil under different microplastic and rainfall levels

表1 微塑料(MP)种类、质量分数和模拟降雨量三因素方差分析结果(F值)¹⁾

Table 1 Significance levels (F value) of microplastic (MP) type, concentration, and simulated rainfall based on a three-way ANOVA

项目	MP质量分数	MP种类	降雨量	MP质量分数×MP种类×降雨量	MP种类×MP质量分数	MP种类×降雨量	MP质量分数×降雨量
浸滤液硝态氮	3.27ns	89.26***	19.05***	0.29ns	1.27ns	11.98***	1.49ns
浸滤液氨氮	0.52ns	3.91ns	5 140.10***	0.82ns	0.03ns	2.54ns	0.23ns
浸滤液总氮	7.82**	24.18***	15.869**	0.33ns	4.28*	15.02***	3.96*
浸滤液总镉	2.98ns	0.14ns	1 785.77***	3.16ns	2.44ns	5.49*	1.04ns
浸滤液无机磷	48.71***	0.05ns	358.83***	7.68**	23.24***	0.05ns	7.03**
浸滤液总钾	4.27ns	0.55ns	117.35***	5.87*	10.39**	2.07ns	1.86ns
土壤总氮	7.86**	0.86ns	26.97***	3.64*	4.45*	2.46ns	55.48***
土壤硝态氮	70.14***	24.00***	206.25***	1.83ns	4.16ns	11.28***	8.67**
土壤铵态氮	20.35***	8.25**	19.74***	12.28***	3.12ns	22.92***	9.29**
土壤有效磷	5.19*	10.29**	2.99ns	0.13ns	0.58ns	0.75ns	1.34ns
土壤速效钾	0.19ns	9.09**	0.87ns	0.06ns	5.99**	0.35ns	0.92ns

1)ns表示不显著,*表示 $P < 0.05$,**表示 $P < 0.01$,***表示 $P < 0.001$

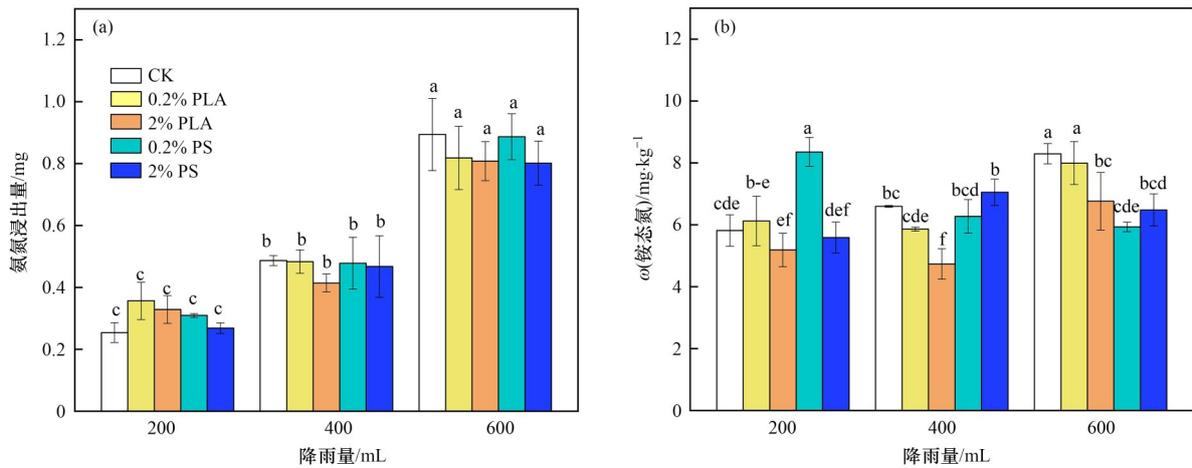


图2 不同微塑料和降雨水平下氨氮浸出量和土壤中铵态氮含量

Fig. 2 Amount of ammonia nitrogen in leachate and ammonium nitrogen content in soil under different microplastic and rainfall levels

含量显著高于低质量分数[图3(b)],分别比对照高27.19%和24.99%。大暴雨量时,微塑料显著降低土壤中总氮的含量,2% PLA最为显著,比对照减少

43.66%。除与微塑料种类和降雨量之间无显著交互作用外,其他交互作用对土壤总氮含量有显著影响(表1)。

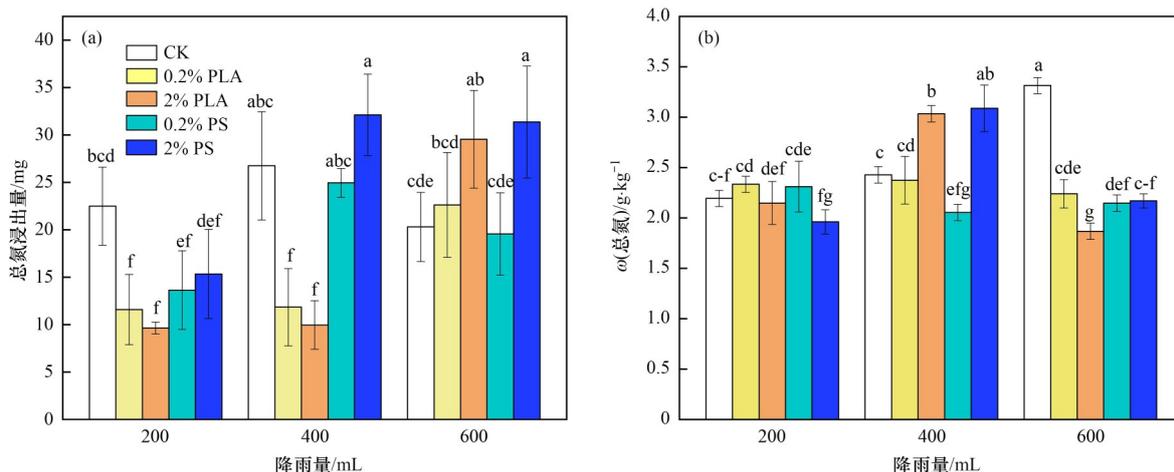


图3 不同微塑料和降雨水平下总氮浸出量和土壤中全氮含量

Fig. 3 Amount of total nitrogen in leachate and total nitrogen content in soil under different microplastic and rainfall levels

2.4 浸滤液无机磷和土壤有效磷

总体上,浸滤液中的无机磷随降雨量增加而增加[图4(a)].大暴雨时微塑料的种类和质量分数都显著影响土壤中无机磷的淋失,其中大暴雨量时2% PS处理比对照显著减少45.31%,而0.2% PS处理比2% PS处理显著增加20.02%.根据三因素方差

分析(表1),除微塑料种类与降雨量无显著交互作用外,其他因素之间均有显著交互作用.不同降雨量对土壤有效磷影响不显著.多数微塑料处理之间没有显著差异.大暴雨量时,与2% PS处理相比,土壤有效磷含量在2% PLA处理中显著降低44.83%[图4(b)].

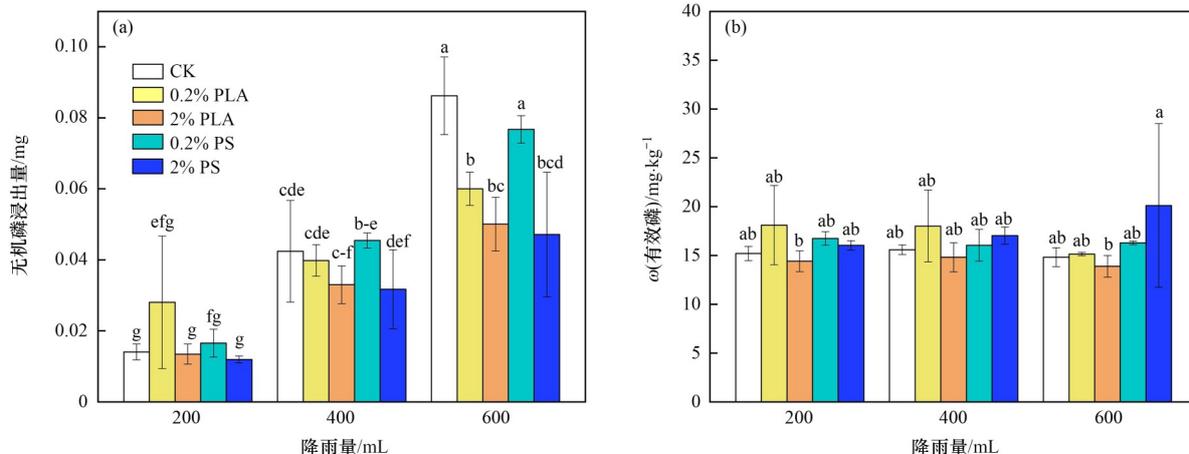


图4 不同微塑料和降雨水平下无机磷浸出量和土壤中有效磷含量

Fig. 4 Amount of inorganic phosphorus in leachate and available phosphorus content in soil under different microplastic and rainfall levels

2.5 浸滤液总钾和土壤速效钾分析

浸滤液中的钾随降雨强度增加而增加,如图5(a)所示.2% PS处理在大暴雨时浸滤液中钾含量比对照显著增加了38.14%.降雨量、微塑料质量分数和种类三者之间对钾的淋失有显著交互作用(表1).与对照相比,大雨量时2% PS处理中土壤速效钾含量增加26.99%[图5(b)].三因素方差分析显示,微塑料种类、微塑料种类和质量分数的交互作用对土壤速效钾含量有显著影响(表1).

2.6 浸滤液总镉分析

随着降雨强度的增加,浸滤液中Cd的含量增加(图6).模拟大暴雨时0.2% PLA处理土壤中Cd淋失

量较显著增加,比对照组高出9.03%.其他降雨量下各微塑料处理之间没有产生差异.三因素方差分析显示(表1),镉的淋失主要受降雨量影响,微塑料种类和降雨量之间对土壤中镉淋失量有弱的交互作用($P < 0.05$).

3 讨论

微塑料会影响土壤的理化性质以及微生物生物群落和功能,但是其效应与微塑料特征(如种类、粒径、剂量、形状、老化程度)、土壤性质(如pH、持水能力、有机质含量、土壤结构)和暴露时间等密切相关^[6,28-30].例如,不同研究发现微塑料对土壤pH影响

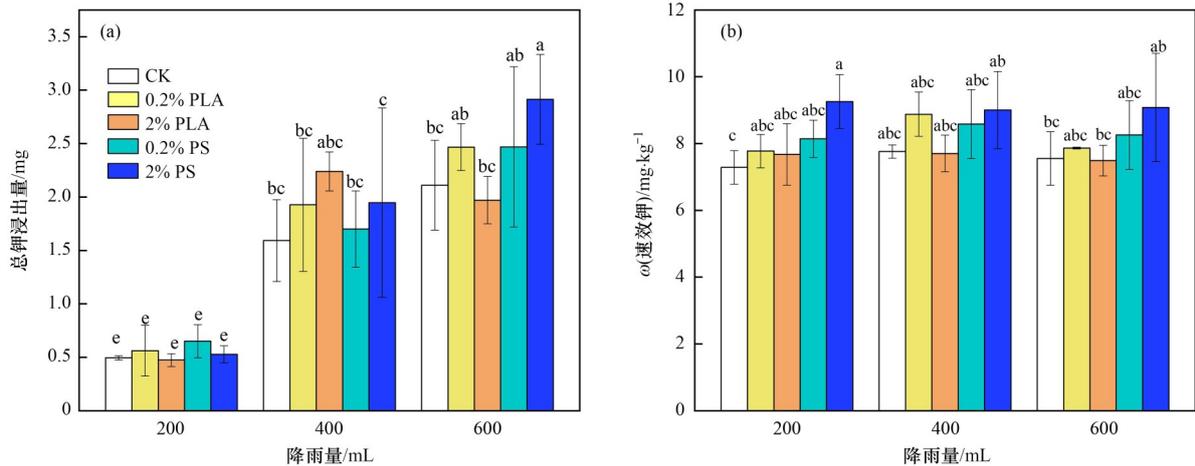


图5 不同微塑料和降雨水平下总钾浸出量和土壤中速效钾含量

Fig. 5 Amount of total potassium in leachate and available potassium content in soil under different microplastic and rainfall levels

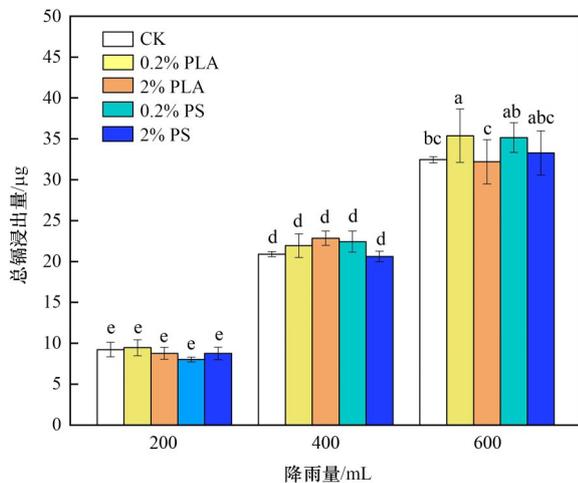


图6 不同微塑料和降雨水平下Cd的浸出量

Fig. 6 Amount of Cd in the leachate under different microplastic and rainfall levels

可能是增加、降低或者没有显著影响^[6,29]。微塑料在土壤中老化会释放出其他物质,进而改变土壤的pH值^[31]。微塑料对土壤特性的影响与微塑料的特征、土壤外部条件以及环境等有关^[6]。聚乙烯(PE)和PLA微塑料在环境温度为25°C时显著降低土壤硝态氮、无机态氮和总可溶性氮含量,并抑制硝化作用和矿化作用,但是在15°C时对氮的转化和有效性影响较小^[32]。笔者最近的研究发现,0.1% PE微塑料使土壤中负责硝酸盐还原、硝酸盐呼吸、亚硝酸盐呼吸和硝酸盐氮化作用的功能菌得到富集,而1% PLA微塑料则使固氮菌的丰度增加,因此微塑料能够通过调控氮循环微生物而对氮循环产生影响^[33]。因此,微塑料对养分和污染物形态的影响是复杂的,难以用单一因素解释^[6]。

降雨会使土壤中的养分通过地表径流或垂直流动,导致土壤中养分流失。强降雨条件下,土壤养分

流失的主要条件是淋溶^[34]。土壤在干旱后经过大雨量渗流,土壤的渗透通量增加,土壤中的氮元素淋失增加^[35]。微塑料在天然的土壤中迁移和归宿受土壤理化性质、离子强度和阳离子类型的影响^[36]。供试土壤pH偏低,微塑料在土壤中的迁移能力较差。跟对照相比,微塑料降低了土壤中铵态氮的含量,增加了总氮的淋失量。这可能是因为微塑料改变了土壤容重、孔隙度和团聚体结构等^[37]。Ingraffia等^[38]发现聚酯微塑料纤维处理的土壤孔隙率增加,在极端降雨时增加氮浸出量。与对照相比,大雨量时微塑料增加了土壤中钾的淋失,使土壤中速效钾含量增加。本研究中微塑料减少了土壤中无机磷的淋失,增加了土壤中有效磷的含量。本研究土壤pH较低,但添加微塑料后土壤的pH略高于对照(结果未显示),这种情况下会影响土壤中有效磷和硝酸盐的含量^[39,40]。Li等^[12]研究发现,微塑料的吸附作用可能不是影响土壤氮磷有效性的决定性因素,更可能是由于土壤团聚体的减少导致土壤对养分的固持能力降低。

本研究发现,镉的淋失主要受降雨影响,但大雨时0.2% PLA增加了土壤中Cd的淋失。土壤中含有多种有机或者无机胶体物质,对重金属的吸附性能较强。虽然微塑料对镉等重金属也具有一定的吸附能力^[41,42],但其吸附容量往往比土壤低,因此微塑料的加入会降低土壤对重金属的吸附性能,增加重金属的解吸^[22]。不同微塑料对镉的吸附能力不同,PLA比PS具有更大的镉吸附容量,但是其解吸能力也强于PS^[43]。微塑料老化会引起表面性质变化,如含氧官能团增加,因此微塑料对镉的吸附能力往往随老化程度而增加^[42]。由于PLA具有可生物降解性,PLA比PS更容易受到环境因素和微生物的影响而逐渐老化和降解,这部分解释了为何0.2% PLA促进了镉淋失。但是,2% PLA却没有显著影响,这可能是因

为 PLA 在高添加量时对土壤性质造成更大的改变。三因素方差分析显示(表 1),总体上,微塑料质量分数和种类对镉的淋失没有显著作用,这一方面可能是因为土壤具有较强的缓冲能力,微塑料的添加没有使土壤性质发生显著变化;另一方面,微塑料对土壤中镉的影响可能源于多种土壤因素的综合作用。长期来看,微塑料(尤其是可降解微塑料)会因老化和降解等作用而改变土壤性质(如 pH、有机质和微生物)^[44,45],并影响土壤养分和污染物的迁移和淋失,这尚需更多深入研究。

4 结论

本研究利用土壤柱实验初步探讨了不同种类和质量分数的微塑料对土壤养分和重金属在土壤中的淋失,包括浸滤液和土壤的硝态氮、铵态氮、总氮、速效钾、有效磷含量以及镉含量。总体上,土壤养分和镉的淋失主要受到降雨的影响,随降雨量增加而增加。微塑料对土壤养分和镉淋失的影响与微塑料的种类和质量分数有关,并受到降雨水平的影响。大暴雨时 2% PS 更能增加土壤中总氮和钾的淋失,大雨时 2% PLA 降低了土壤硝酸盐含量,大暴雨时减少无机磷的损失。大暴雨时 2% PS 增加土壤中有效磷含量,大雨时 2% PS 增加土壤速效钾含量。大暴雨时 0.2% PLA 显著增加土壤中镉的淋失。本研究可为认识可降解塑料和不可降解塑料在土壤中的环境风险提供一定依据。

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