

陆地生态系统中水溶性有机质的环境效应

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摘要: 目前水溶性有机质(Dissolved Organic Matter)已逐步成为陆地生态系统中的一个研究热点。系统地评述了陆地生态系统中DOM 的组成特点及其环境效应。尽管关于陆地生态系统中DOM 的研究还不完善, 至今对其性质、组成和分类方法等问题看法不一, 但现有结果已经表明DOM 是一种十分活跃的重要化学组分, 它对陆地生态系统中污染物质的溶解、吸附、解吸、吸收、迁移和生物毒性、微生物活动以及土壤形成过程等均有显著的影响。影响DOM 在陆地生态系统中的环境效应的主要因素包括: DOM 与污染物的络合作用、污染物溶解/沉淀作用、土壤对DOM 的吸附作用、土壤质地、酸碱缓冲作用等。

关键词: 水溶性有机质(DOM); 陆地生态系统; 重金属; 有机污染物; 环境效应

Environmental Effects of Dissolved Organic Matters in Terrestrial Ecosystems: a Review

HUANG Ze-Chun, CHEN Tong-Bin, LEI Mei (Lab. of Environmental Remediation, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China). Acta Ecologica Sinica, 2002, 22(2): 259~ 269.

Abstract Researches on dissolved organic matters (DOMs) have been increasing in water and soil studies since the concept of DOM was proposed in 1970's. Although most former researchers considered that humic substances might substitute soil organic matters in liquid phase, more and more later studies made sure that DOMs, which were water extracted, could represent soil organic matters in liquid phase more properly than humic substances. Results of IR, NMR, RPLC and other spectrum analyses revealed that there were great differences between DOMs and humic substances. In contrast with DOMs, humic substances contained less hydrophilic and acid organic matters, which were the essential components of soil organic matters. Components, characters and environmental effects of DOMs in terrestrial ecosystems were reviewed in this paper.

It was difficult to identify all the components in DOMs, which were complex organic mixtures in ecosystems. In order to understand the characters and components of DOMs, spectrum analyses methods were introduced to resolve the chemical groups in DOMs. Hydroxy, carboxyl, phenyl and some other groups were discovered in DOMs. Information about groups and their content would help to infer possible components in DOMs, but it was too sketchy to know the characters of DOMs. Classifying the components of DOMs according to some chemical or physical properties was needed to study most complex mixtures such as DOMs. Properties concerned in classification include: elements, functional groups, special compounds, molecular weight, polarity, acidity, and so on. Among them, molecular weight or polarity and acidity was the most commonly used in classification. Lots of information about components and chem-

基金项目: 北京市自然科学基金重大资助项目(6990002); 中国科学院知识创新工程重要方向资助项目(KZCX2-401); 国家自然科学基金资助项目(049671003)

收稿日期: 2001-02-07; **修订日期:** 2001-11-30

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ical characters of DOMs has been acquired based on classification, which also provided a valuable way to compare DOMs extracted from various sources or by different means. Although most of the information of the components of DOMs was known by classification, the grade of classification was different for every researcher according to their researching object, and the result of classification was difficult to be compared with each other. More attention should be paid to the study of classification.

DOMs in terrestrial ecosystems might be naturally derived from biomass decomposition and soil solid organic or manually imported by wastewater irrigation. DOMs from both sources have great effects on the behaviors of metals in terrestrial ecosystems. Earlier researchers found that DOMs in soils under conifer forest might play an important role in soil podzolization. The main mechanism in this process was that DOMs might complex with Al and Fe, which would result in enhancing their mobility and leaching ratio. The effects of chelators and ligands on the solubility, adsorption, desorption, transportation and toxicity of metals in soil was well known. DOMs contained a lot of ligands could also complex with heavy metals and affect their behaviors in soils. Two main processes would happen when DOMs were added into soils: complexing with heavy metals in soils or adsorbed on soils. Factors that would affect those two processes were summarized as follow:

Complexing of DOMs with heavy metals, which was mainly controlled by the affinity of DOMs and heavy metals, would enhance the solubility and reduce the adsorption of heavy metals on soils. Both the components of DOMs and heavy metals determined the affinity of DOMs and heavy metals. It was shown that DOMs might reduce the adsorption of Cu greater than Cd, which might mainly ascribe to that Cu combined with DOMs stronger than Cd. That's why most of recent researches on the effects of DOMs concerned in Cu. The component of DOMs could also affect the affinity to heavy metals. It was shown that DOMs with lower molecular weight components would reduce the adsorption of heavy metal on soils greater than DOMs with lease low molecular weight components.

Adsorption of DOMs on soils would have two main influences: competing the adsorption point of metals that would reduce the adsorption of heavy metals in soils, or acting as a bridge between heavy metals and solid phase that would enhance the adsorption of heavy metal in soils. It was shown that DOMs might enhance the adsorption of heavy metals in acid soils, which might due to that DOMs with negative charge can neutralize the positive charge in acid soils and enhance the adsorption of cation with positive charge. The adsorption of DOMs on soil might also affect the pH of soils that was an important factor in the adsorption of heavy metals.

Except of the factors mentioned above, the texture of soils could also lead to the different effects of DOMs on heavy metal in different soils. The combined action of all those factors would eventually determined the effects of DOMs on the behaviors of heavy metal, but which acted as the main factor was determined by given situations, and should be clarified respectively.

The effects of DOMs on pollutants were also concerned by lots of researchers. DOMs could affect participation, mobility and bioavailability of hydrophobic organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), napropamide, atrazine and DDT in soils and sediments. Although a lot of experiments proved that DOMs could reduce the adsorption of organic chemicals in soils and enhance their mobility, the mechanisms in those processes have not been fully elucidated. Chiu (1986) suggested that DOMs might reduce the adsorption of organic pollutants through increasing the distribution of organic pollutants in liquid phase. But some other researchers considered that the main mechanism was that organic pollutants might complex with some sections of DOMs.

Studies in DOMs in terrestrial ecosystems have been the hotspot abroad, but it was still less in China.

Along with the application of organic manure and wastewater irrigation, the effects of DOMs on the behaviors of pollutants has been paid more and more attention. DOM might even cause secondary pollution in contaminated soils. More researches should be conducted to study the effects of DOMs and the mechanisms in those processes.

Key words: dissolved organic matter (DOM); terrestrial ecosystem; heavy metals; organic pollutants; environmental effect

文章编号: 1000-0933(2002)02-0259-11 中图分类号: Q 148, S154, X171, X53 文献标识码: A

水溶性有机质(Dissolved Organic Matter)是土壤和自然水体中的一种常见组分^[1~3],它对陆地生态系统有多方面的影响。土壤中DOM可以通过pH缓冲作用、络合螯合作用影响土壤溶液的化学性质^[4]。最新研究表明,DOM比固相有机质具有更多的活性点位^[5]。同时,由于其具有水溶性的特点,因此被认为是陆地生态系统和水生生态系统中一种重要的、活跃的化学组分。DOM在自然环境中,不仅可以影响污染物(重金属、农药)和C、N等元素的迁移能力和生物有效性^[6,7],而且还是风化和成土过程的重要影响因素。本文主要评述DOM的组成、特点及其生态环境效应。

1 DOM的组成

DOM的化学组成对其在陆地生态系统中的功能和行为有很大的影响。但是由于DOM是一种非常复杂的包含一系列化学性质各异的化合物的混合物,确定DOM的组分相当困难^[8]。目前,对于DOM组成的认识大多基于光谱学分析和分组考察的结果。

1.1 DOM的化学结构特征

许多研究者采用了红外光谱(IR)、核磁共振光谱(NMR)^[2]等有机结构分析方法,分析DOM的结构特征。M agee等^[9]IR分析的结果表明,土壤中的DOM主要含有羟基、芳香基、羧基。Baham等^[10]采用IR分析污泥DOM发现,在污泥DOM中酸水解产物的成分占55%。其中 α -氨基占26%,氨基己酤占9%,中性糖残渣占12%,脂肪族占8%。Kaiser等^[11]采用漫反射傅立叶转换红外光谱(DRIFT)分析土壤中天然DOM的结构(表1)。

表1 DRIFT对土壤中天然DOM结构分析的结果^[11]

Table 1 Major peaks in DRIFT spectroscopy and corresponding molecular structures of natural DOM exacted from soil		
波数(cm^{-1}) DRIFT bands	相应的化学基团	Assignment
1720~ 1710	羧基上的C=O	伸缩振动
1625~ 1600	芳香基上的C=C	伸缩振动或羧基上的不对称伸缩振动
1510	芳香基上的C=C	伸缩振动
1470	—CH ₃ 上的C—H	变形振动, —CH ₃ 、—CH上的弯曲振动
1400	羧基上的不对称伸缩振动, 羧基上的C—OH	变形振动, 脂肪族—CH上的弯曲振动
1270	酚羟基上的C—OH	伸缩振动
1240~ 1200	羧基上的C—O	不对称伸缩振动, 羧基上的C—OH 变形振动
1170~ 1150	脂肪族上的C—OH、C—O	伸缩振动
1050~ 1020	酚类或醇类上的C—O	不对称伸缩振动

通过这些有机结构分析方法,虽然无法得到DOM的详细化学组成,但其所反映的DOM含有的化合物的官能团组成及其比例的信息,对于了解DOM性质和其在生态系统中的功能具有很重要的意义。

1.2 DOM的组分与分级

在定量或定性描述DOM的特征时,往往通过描述各组分及其组成比例来刻画DOM的总体性质,以及对比不同种类DOM的差异。DOM主要的分组方法有:按元素和官能团分组、按特殊化合物或化学基团分组、按分子量分组、按亲水性分组、按酸碱性分组等^[2, 12]。

1.2.1 按分子量分级 按DOM组分的分子量大小进行分级,是常用的描述DOM性质的分级方法。通常认为,分子量大小是影响DOM性质的主要因素。同一DOM中,分子量不同的组分化学性质不同,

在土壤中的迁移能力及其金属离子结合能力也不同^[4, 13]。McCarthy等实验结果表明^[14],在土壤含水层中,低分子量(< 300MW)的DOM的迁移能力大于大分子量(> 300MW)的DOM。按分子量来分级常用的方法有:凝胶渗透色谱分析^[15, 16]、膜透析^[17]、超滤^[2, 14]等方法。

Baham 等^[10]对厌氧消化污泥中提取的水溶性有机络合物采用凝胶渗透色谱(SepHdex G-10)进行分级;其中分子量< 700、700~ 1500 和> 1500 道尔顿的组分分别占 24%、22.5% 和 43%。McCarthy 等^[14]将表土的天然 DOM 分为 3 部分:分子量< 3000MW 的组分主要是低分子量有机物质,其中包含富里酸;3~ 100K MW 的组分为有机大分子;> 100K MW 分子量级别的含量较少。Homann 等^[17]采用膜透析法和超滤法两种方法对森林土壤中 DOM 分类的结果基本一致,将土壤中提取的 DOM 分成 3500、12000、14000 道尔顿等级别,其中高分子量(> 14000 道尔顿)的 DOM 组分占 DOM 的大部分^[17]。

众多的研究者采用了分子量分级方法研究 DOM 组分,一方面表明了分子量分级方法是认识 DOM 性质的重要手段;另一方面,由于各研究人员采用的实验方法的不同,以及划分分子量级别上认识的差异,使得研究成果之间缺乏可比性。

1.2.2 按极性和电荷性质分级 从 DOM 组分的亲水性、酸碱性这两种化学性质出发,对 DOM 进行分组考察,也是当前研究 DOM 性质的常用方法之一。这种方法最早由 Leenheer 和 Huffman^[12]率先提出,之后又有众多研究人员^[18~ 20]采用该方法对 DOM 进行分组。虽然,各研究者在分组的操作上略有不同,采用的树脂型号也有区别,但是其主要的操作步骤基本类似。光谱分析表明,各组分之间在化合物组成上存在很大的差异:亲水的酸性组分主要包含生物氧化物和腐殖质类小分子物质;亲水的中性组分主要包含多糖和多糖醛酸苷;亲水的碱性组分主要包含蛋白质和缩氨酸、氨基糖等氨基糖生物多聚体;疏水的酸性组分主要包含单宁、多酚、氧化多酚、与腐殖质结合的碳水化合物;疏水的中性组分主要包含碳水化合物、长链脂肪酸、烷基醇和少量腐殖质;疏水的碱性组分主要包含芳香族化合物、石蜡族化合物、碳水化合物和胺^[8]。

2 DOM 与腐殖酸类物质的联系与区别

对于天然水体及土壤中的有机物研究,过去大多都集中在腐殖质方面。DOM 与腐殖质的提取方法不同,两者在化学组成上也存在差异。Baham 等认为^[10],水浸提法对蛋白质提取较为有效,而对碳水化合物的提取效率较低。用水提取的有机质较富里酸含氮较多,可能富含 C/N 比较低的有机聚合物——多肽、氨基糖、含氮碱。

广义而言,腐殖酸也属于特殊的可溶性有机质,或碱溶性有机质。Grasso 等^[7]认为,DOM 组分中大约 25%~ 50% 由腐殖酸和富里酸组成,其余的组分主要是蛋白质、多糖和亲水性有机酸。Homann 等认为^[17],DOM 中分子量小于几千道尔顿的成分主要包括脂肪酸、芳香酸、氨基酸、单糖、低聚糖和低分子量的富里酸,而高分子量的 DOM 主要包括结构复杂的物质,如高分子量的富里酸和胡敏酸。

腐殖酸与用水提取的有机质在 pH= 2~ 10 之间均保持真溶液状态^[10]。由于腐殖酸的可溶性,有人认为它与用蒸馏水浸提的 DOM 至少在性质上有相似之处。在实验室中,商品腐殖酸也常作为天然 DOM 的替代品。但是另有许多研究人员根据红外光谱、色谱及核磁共振等方法的研究结果对这种做法提出质疑^[7]。他们发现,虽然腐殖酸与用水提取的 DOM 有部分相同的吸收峰,但是用蒸馏水提取的 DOM 与自然条件下土壤中的液相有机质在化学组成上更加相似,而传统意义上的腐殖酸类物质与 DOM 之间有着明显的区别。

2.1 化学结构的差异

腐殖质的主要官能团有:羧酸、酚基、羟基和酮基。通常认为富里酸有两种官能团:水杨酸基和二羧酸基^[21]。Grasso 等^[7]采用 ¹H-NMR 分析了通用商品腐殖酸和两种从天然水体中分离出来的 DOM,其分析结果见表 2。

从表 2 对比上看,虽然不同的 DOM 在分子结构和官能团的组成上也存在差异,但 DOM 和腐殖酸在分子结构和官能团的组成上的差异更为明显。

2.2 极性的差异

反相液相色谱(Reverse Phase Liquid Chromatography)主要用于分离不同极性的组分,化合物的极性越强,在 RPLC 中的保留时间就越短。对商品腐殖酸和两种从水体中分离的 DOM 的 RPLC 分析结果发现^[7],两种 DOM 的出峰时间较短,说明其组分中主要是亲水性成分;而在商品腐殖酸的图谱中,亲水性成分峰值较低,而且含有大量的非极性峰。

表 2 腐殖酸和 DOM 的 ¹H-NMR 测定结果^[7]

Table 2 Major peaks in ¹H-NMR and possible molecular configuration of aldrich humic acid and DOM from two natural sources

化学位移 Chemical Shift	对应的官能团 Assignment	AHA	HRW	LMPW
0.8~1.0	直链烃末端的甲基基团	0.8~1.11	0.7	无
1.0~1.4	芳香环上 β 或 γ 位甲基	1.11	1.15+1.14	无
1.4~1.7	脂环族的亚甲基	1.7	无	1.5+1.6
1.7~2.0	芳香环上 α 碳	2.0	1.73	无
2.0~3.3	芳香环 α 位脂肪族支链; 羰基、羧基 α 位脂肪族支链	2.4~2.7	2.5~3.3	2.7+
3.3~5.0	甲氧基、醛基与氧相连的 α 烃基; 芳香胺、碳水化合物, 芳香羟基聚合体、内酯、酚基上的可交换 H、羧基	无	3.1~3.4 3.5~3.9 4.0~4.4	3.0~3.9 4.3~4.6
6.5~8.1	芳香环(包括酚和醌)上无空间阻碍(unhindered)的 H	7.0~8.6	无	无
8.1~9.0	在空间上受到阻碍的 H、氮的芳香族衍生物、甲酸盐	8.3~8.6	无	无

* AHA: Aldrich 腐殖酸; HRW: Huron River 河水中提取的 DOM; LMPW: Michigan 湖孔隙水中提取的 DOM

2.3 分子量组成的差异

Grasso 等^[7]通过对商品腐殖酸和两种从水体中提取的 DOM 进行凝胶渗透色谱(gel permeation chromatography)分析的结果表明,在图谱上商品腐殖酸有 3 个峰,而两种 DOM 却都只有两个峰。

从化学结构、极性和分子量组成等方面都说明了,DOM 和腐殖酸在各方面存在很大的区别。早期的从事土壤腐殖酸研究的工作往往忽略了亲水部分和碱性部分。直到 20 世纪 70 年代,随着 DOM 这一概念提出并不断对其进行探索,才逐渐认识到用腐殖酸来替代自然土壤中的液相有机质来开展研究工作,与实际情况有很大的差异。

3 陆地生态系统中 DOM 的作用与功能

3.1 DOM 对土壤形成过程的影响

很早以前就有人认识到,天然 DOM 对土壤中金属离子迁移有明显的影响,DOM 的酸性基团与金属发生络合作用,从而影响矿物的风化作用^[22]。其中主要的研究方向是对土壤灰化作用和致酸离子(A1、Fe)淋溶的影响。DOM 对诸如灰化作用的成土过程有重要的影响^[4,23]。在北方生物带,DOM 在针叶林土壤形成过程中起着重要作用。金属离子在土壤剖面的淋溶作用与溶解性有机碳(Dissolved Organic Carbon)有很大关系^[24]。在灰化土剖面表层(5~20cm)的渗滤水中,可溶性 A1 与 DOM 浓度呈正相关,而且灰化土表层中大部分 A1 以有机态存在^[25]。大部分的研究者认为 DOM 影响土壤成土过程的主要作用机制是,森林土壤枯枝落叶层和有机质层中有机质降解产生的 DOM,包含亲水性有机质、疏水性酸和碱以及包含大量单宁的多酚类物质,这类物质可以与土壤矿物中的 A1、Fe 发生螯合作用,促进土壤中 Fe、A1 的解吸和溶解^[18,24,26]。

3.2 DOM 对土壤中重金属环境行为的影响

络合作用对土壤中重金属吸附行为的影响,很早就有相关的研究工作。很多人在研究土壤重金属有效态的提取方法中都发现,络合剂可以提高土壤中重金属的可溶性^[21,27~30]。Gardiner^[28]、Papassopi 等^[29]实验发现,EDTA 可以提高土壤中 Cd 的解吸率或 Cd 的溶解度。由于 DOM 也含有大量的络合/螯合基团,同样也可以与土壤中的重金属通过络合和螯合作用,形成有机—金属配合物。有机酸、腐殖酸类物质和 DOM 等,在环境中都以可溶性的络合剂形式存在。它们通过与水体、土壤和沉积物中的金属离子、氧化物、矿物和有机物之间的离子交换、吸附、络合、螯合、絮凝、氧化还原等一系列反应,改变重金属的生物毒性、迁移转化规律与最终归宿^[31~33]。

DOM 对污染物起着迁移载体的作用,是促进许多污染物向地表水体或地下水体迁移的重要因素^[34~41]。DOM 对土壤重金属有很强的解吸作用,在含水多孔介质和地下含水层中,DOM 对重金属淋溶的促进作用尤其明显。含水砂层中微生物代谢产生的 DOM 仅 10 mg/L 便可使 Cd、Pb 的吸附能力分别降

低 90%、60%^[41]。因此某些情况下,可能会造成重金属毒害及其在环境中扩散的加剧^[14, 18]。Lamy 等发现^[42],在施用污泥的土壤中,土壤深层水或土壤排水中的重金属浓度与其 DOM 浓度呈显著正相关。

DOM 对土壤中重金属的影响形式有:有机络合剂可以通过与液相金属离子竞争吸附点位或优先吸附在固体表面上,减少了重金属的吸附点位,从而降低土-水系统中金属离子的吸附作用^[42];另一方面,可以作为土壤与金属之间的络合桥梁增强固体表面的亲和力,从而增加金属的吸附^[34, 43];与重金属离子形成络合物,抑制土壤中重金属的吸附作用,提高重金属的迁移能力^[41, 44, 45]。

综上所述,DOM 对土壤中重金属吸附、解吸(溶解)、迁移的影响,是一系列复杂反应的综合结果,重金属的吸附势是由该重金属与 DOM 和与土壤固相结合两种作用共同决定的^[46]。其主要的影响因素包括以下几个方面。

3.2.1 络和作用的强度 DOM 对重金属在土壤中吸附的影响,与该元素和 DOM 结合的稳定性有关。Inskip 等认为^[47],DOM 使蒙脱石表面 Cu^{2+} 吸附量明显降低,但对 Cd^{2+} 的吸附量的影响较小。Kalbitz 等^[45]对湿地中重金属的迁移能力与 DOM 的相关分析,表明 Hg、Cr、Cu、As 的迁移能力与 DOM 浓度呈正相关,而 Cd、Zn 的迁移能力与 DOM 浓度相关性不显著。Kuiter^[4]研究表明,往土壤中加入柠檬酸、草酸、水杨酸、原儿茶酸等低分子量有机酸,对土壤溶液中 Zn 浓度的影响不大,Fe、Al、Cu、Pb 浓度增大,Ca、Mg 浓度减小。在保持 pH 不变的情况下,随着 DOM 加入量的增大,土壤溶液中 Al、Fe、Cu 的浓度都相应增大,其中 Cu 最为明显。这些实验结果都反映了,DOM 对重金属的环境行为的影响与元素有关,而其中主要的影响因素可能是 DOM 与重金属元素的络合能力的差异。一般认为,在重金属中 Cu 与有机质的络和能力较强^[5],因此,针对 DOM 与重金属吸附的关系问题,大量研究都集中在 Cu。Lehman 等认为^[38],不管在任何氧化-还原条件下,DOM 都使 Cu 的迁移能力大大增加。Sebastien 等^[48]研究结果表明,DOC 含量增加 300% ~ 400%,可溶性 Cu 增加 400% ~ 500%。

另外,DOM 与重金属的络和能力还与 DOM 的性质和组成有关。陈同斌等^[44]研究结果表明,经过堆腐污泥 DOM 对 Cd 吸附的抑制作用要比未经堆腐处理的污泥 DOM 以及小麦秸秆 DOM 强,其可能原因与堆腐过程中产生的络和能力较强的小分子有机物有关。Zhou 等^[36]在研究中也发现,Cu 与 DOM 的络和能力随着 DOM 分子量的增加而显著降低,并认为其主要原因是小分子 DOM 与大分子 DOM 相比具有更多的结合点位。另外,Chafetz 等^[81]的研究结果认为,在污泥堆肥过程中 DOM 的疏水性组分的增加,能促进 DOM 与 Cd 的络合作用。

3.2.2 DOM 在土壤中的吸附 研究发现^[46],土壤溶液中的 DOM 也会在固、液两相之间发生分配。DOM 能很快被土壤吸附,在几小时后即可达到平衡。DOM 被土壤矿物强烈吸附,通常导致土壤中 DOM 浓度较低^[15]。DOM 在土壤中的吸附,改变了土壤矿物表面的吸附点位和电荷等性质,这可能是 DOM 促进重金属吸附的重要机制之一。Moore 等发现^[23],酸性土壤对 DOM 的吸附能力较强,认为其主要原因是,在较低的 pH 条件下,土壤表面带有很强的正电荷,能促进带负电荷的络合剂的吸附。这种吸附作用导致土壤负电荷增加,从而促进带正电荷的重金属的吸附。另外,有些重金属的有机复合物与土壤矿物的亲和力大于游离态离子,这种可溶性有机-重金属复合体被土壤吸附后可以促进重金属的吸附。吴龙华等^[34]研究发现,猪粪 DOM 的浓度增大到一定程度时可以促进 Cu 的吸附,这可能与土壤 DOM 复合体的形成有关。因此,DOM 促进重金属的吸附可能是通过 DOM 改变土壤表面的电荷性质或形成(土壤-络合剂-金属)复合体的缘故。

3.2.3 土壤质地 DOM 作为有机配位体,既可以与重金属离子作用,又可以与土壤、矿物表面作用,因此土壤质地与 DOM 对重金属吸附行为的影响有很大的关系^[34, 47, 49, 50]。在不同的土壤矿物中有机酸对重金属吸附作用的影响存在很大差异:腐殖酸可以促进 $\text{Al}(\text{OH})_3$ 、 $\text{Fe}(\text{OH})_3$ 对 Cd^{2+} 的吸附,而降低高岭石和蒙脱石对 Cd^{2+} 的吸附^[43];Pb 在砂土中的吸附量随腐殖酸的增加而微弱减少,而在高岭土中腐殖酸的作用相反^[49]。王果等^[50]对红壤和潮土两种土壤的研究结果发现,在相近的土壤 pH 条件下,红壤中稻草水溶性分解产物对 Cd 吸附的促进作用大于猪粪,在潮土中两者没有很大差异。黄泽春等^[51]发现,TOC 含量高的土壤中 DOM 对 Cd 吸附的抑制作用更强。这些实验结果都表明了,DOM 对土壤重金属环境行为的影响与土

壤质地有很大的关系。

3.2.4 土壤 pH 和 DOM 酸碱缓冲作用 土壤中 DOM 可以通过对 pH 的缓冲作用等影响土壤溶液的化学性质^[4]。陈同斌等^[44]研究结果表明, DOM 可以使酸性土壤的 pH 升高, 使碱性土壤的 pH 降低。Kaiser 等认为^[6], DOM 影响土壤 pH 的主要机制是, DOM 与土壤表面的羟基发生阴离子交换作用。

研究发现^[42, 51], 在酸性介质中, 城市污泥 DOM 可促进土壤中 Cd 的吸附, 而在碱性介质中则相反。陈同斌等曾^[52]研究塘泥和稻秆 DOM 对水稻土 (pH = 5.85)、赤红壤 (pH = 6.14)、褐潮土 (pH = 7.95) 3 种土壤中 Cd 吸附的影响, 发现 DOM 在 3 种土壤中的抑制作用由强到弱为: 褐潮土 > 赤红壤 > 水稻土。王果等研究发现^[50], 红壤和潮土中加入猪粪、紫云英、稻草等有机肥的分解产物会促进 Cd 的吸附。其主要原因是有机分解产物的加入导致平衡溶液 pH 的升高, 抵消有机肥分解产物对 Cd 吸附的抑制作用。3 种有机肥分解产物对潮土中 Cd 吸附的影响与平衡溶液 pH 的差异顺序相符, 也说明了 DOM 酸碱缓冲作用的影响。DOM 对土壤溶液 pH 的缓冲作用也影响其自身与重金属的结合能力^[30]。Lamy 研究表明^[42], 与 DOM 结合的 Cd 与 pH 之间的关系曲线在 pH = 5~7 之间达到峰值。在此 pH 范围内, 加入 DOM 降低了土壤对 Cd 的吸附能力, DOM-Cd 占总 Cd 的 12%。

3.2.5 改变重金属的溶解度 DOM 对重金属沉淀的溶解作用也是抑制重金属吸附的重要机制。DOM 可以与重金属形成螯合物^[53], 从而影响沉淀颗粒的生长、絮凝、凝结和溶解等表面反应^[9], 进而提高重金属在土壤中的溶解度^[54]。Ravichandran 等认为^[55, 56], DOM 可以抑制 HgS 的沉淀, 提高其溶解度。Bingham 的实验表明^[57], DOM 抑制 HgS 沉淀生成的能力随 DOM 浓度的增加而升高, 当 DOC 达到 3~4 mgC/L 时抑制效果达到最大 (100%)。另外, 土壤中的 DOM 也会因为絮凝反应和微生物作用影响重金属的溶解度。Petrovic 等发现^[49], 在富里酸浓度较高 (> 100 mg/L) 时, 容易形成 ML_n 型有机-金属化合物, 使富里酸易形成难溶性胶体, 进而形成更大的絮状物, 导致有机-金属复合物的沉淀。Sebastien 等^[48]发现随 DOC 的增加, 可溶性 Cu 有减少的趋势。其主要原因是: 微生物的活动降低了氧化还原电位, 提高 S^{2-} 的浓度, 导致 CuS 沉淀。

3.3 DOM 对疏水性有机污染物环境行为的影响

土壤和沉积物环境中, DOM 可能对疏水性有机污染物的分配、迁移和生物有效性均起着控制作用。天然 DOC 或腐殖酸与氯苯和 PCBS 等疏水性有机污染物结合, 不仅可以控制其在水中的分配, 而且可以影响其生物富集系数^[58~60]。Marschner 发现^[61], 土壤溶液中存在的 DOM 可以影响 PAH 和 PCBS 在土壤表面的吸附。平衡吸附和土柱实验表明, 污泥中的 DOM 可以与农药结合, 显著促进草萘胺等农药在砂土中的迁移^[62]。Chiu 等发现^[63], 水溶态腐殖酸能促进疏水性的杀虫剂阿特拉津在土壤中的解吸。

DOM 对有机污染物的影响与 DOM 的组分和有关。Hassett 指出^[64], 有机质 (水中的胡敏酸) 的分子量也影响 PCBS 吸附。当有机质的分子超过 50000 道尔顿时, K_{oc} 明显提高。Pedersen 等^[65]发现, 分子量大于 10000 道尔顿时和小于 1000 道尔顿时 DOM 对 TeCB 的分配系数影响最大。Scharpenseed 等也曾提及^[66], PCBs 在 HA 上的结合比在 FA 上的结合稳固。液态污泥、固态污泥和经过石灰稳定处理的污泥中的 DOM, 可以在水中与阿特拉津结合, 从而降低土壤对阿特拉津的吸附; 但与此相反, 污泥堆肥中的 DOM 则与阿特拉津在土壤固相上结合, 因此促进土壤对阿特拉津的吸附^[67]。

DOM 有机污染物环境行为的影响, 大部分都集中在腐殖酸类物质上, DOM 对有机污染物的影响机理的研究也大多借鉴腐殖酸研究的结果。部分的研究人员试图用分配理论来解释土壤中的 DOM 对有机污染物环境行为的影响^[63, 68], 但是其它一些研究人员在研究中发现在一些有机污染物中 DOM 的影响与分配理论不附^[16, 65], 提出 DOM 的一些特殊作用的基团与有机污染物的结合是 DOM 的主要作用方式。目前 DOM 对有机污染物的环境行为影响的影响机制以及 DOM 与有机污染物的结合方式还不清楚, 都有待于进一步的研究。

4 结语

DOM 这一概念在 20 世纪 70 年代才提出, 并开始不断对其进行探索。80 年代以后, 国外有关 DOM 的文献报导急剧增加, 但是我国至今仍极少开展深入的研究^[69]。尽管近些年来有关 DOM 和重金属相互作用

的研究已经不断增多,但大部分都是研究陆地生态系统中天然来源的 DOM 对土壤中重金属吸附/解吸的影响。各种有机肥料(家畜粪便、绿肥、秸秆)和污泥也是陆地生态系统中 DOM 的重要来源^[16, 22],这些人为引入的 DOM 对土壤中重金属和有机污染物环境行为的影响及其机理的研究还鲜有报道。富含有机质的废弃物,可以导致水溶性有机质增加,其结果可能导致污染物在土壤中的活性和迁移能力的提高^[31, 70],从而间接导致土壤污染程度的扩大,并引发二次污染。这些方面的研究工作都有待进一步开展。另外,DOM 对植物生长、微生物活动以及 CO₂ 排放均有一定影响。总而言之,目前关于陆地生态系统中 DOM 的生态环境效应研究,已越来越成为农业环境保护、生态学和全球变化等领域的研究焦点。

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