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土壤中硒的生物有效性表征方法及影响因素研究进展

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摘要: 硒是人体必需的微量元素之一。土壤-植物体系是人体摄入硒的主要途径,但尚缺乏准确评价土壤中硒生物有效性的通用方法,且影响因素也复杂多样,这些问题制约了富硒土地资源的利用。本文通过追踪近年来国内外研究成果,系统地总结及比较了化学提取法、梯度扩散薄膜法、区域尺度硒生物有效性评价方法的优缺点。传统的化学提取法如单一提取和顺序提取在一定程度上能够表征土壤中生物有效性硒,但提取过程中存在影响因素多和提取不完全等问题。梯度扩散薄膜技术(DGT)能够模拟植物的根系吸收过程,相比顺序提取能更好地表征硒的生物有效性,但由于复杂的自然体系和不同元素结合相的差异,野外原位表征技术上仍存在难度。通过大规模的农作物-根系土样本,建立土壤-农作物硒元素评价模型,模型参数为影响土壤硒有效性的理化指标(如土壤酸碱度、有机质含量、土壤硒总量等),能较好地预测区域尺度上硒生物有效性。本文还总结了影响植物吸收土壤中硒的因素如地形、土壤类型、硒的存在形态、土壤理化性质、植物种类、土壤老化等,认为地形和土壤类型、硒的存在形态、酸碱度和有机质是影响有效硒的主要因素,植物种类与土壤老化为次要因素。完善 DGT 等原位分析检测技术、改进元素形态分析方法是未来发展的重要方向。

关键词: 硒; 土壤; 生物有效性; 影响因素; 化学形态; 表征方法

要点:

(1) 化学提取法和梯度扩散薄膜技术在表征硒生物有效性上仍存在不足。

(2) 区域尺度土壤硒的生物有效性评价模型预测的成功率较高。

(3) 成土母质及土壤理化性质是影响植物吸收土壤硒的主要因素。

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硒是一种自然界中含量很低的类金属元素,广泛存在于岩石、矿物、土壤、火山物质、硫和硫化物的沉积物、煤和煤灰以及灰尘中[1]。硒作为动物生长所必需的微量元素之一,对人体和动物健康都有重要的影响[2-5]。全球土壤中的硒分布不均,浓度差别较大,范围主要在 0.01~2.0mg/kg 之间,地壳中

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硒的平均丰度为 0.07mg/kg,但在一些富硒区可以达到 1200mg/kg[6]。Dinh 等[7]对中国环境中硒的分布进行了统计,土壤硒浓度变化范围为 0.005~79.08mg/kg,约有 51%的土壤缺硒。而在湖北恩施、陕西紫阳土壤富硒区域,土壤硒含量最高分别可达 79.08mg/kg、36.69mg/kg,平均含量分别为 27.81mg/kg、17.29mg/kg,呈带状或点状分布[8]。人体硒缺乏与硒中毒之间范围很窄,仅为 40~400μg/d,缺硒或摄入过量均对人体有害[9]。

人体摄入的硒主要来自于植物性膳食,植物可食用部分的硒含量与土壤硒含量密切相关[10-12]。植物对元素的积累并不简单地取决于元素在土壤中的总含量,主要与元素的生物有效性密切相关[13-14]。硒在土壤中进行着复杂多样的化学反应过程,这些反应过程直接影响着硒的生物有效性[15]。因此,准确地评价土壤硒的生物有效性及其影响因素具有非常重要的意义。前人针对化学提取法等方面开展了大量的工作,但还存在提取专一性不足和提取过程中硒形态转化的问题[16-17]。当前的生物有效性表征方法还不能完全满足富硒土地资源调查评价需求[18]。

本文总结了土壤硒的生物有效性表征方法,包括化学形态法、梯度扩散薄膜法、区域尺度硒生物有效性评价方法,分析了不同方法的优点和局限性;讨论了地形和土壤类型、硒的存在形态、土壤 pH、土壤有机质、植物种类和土壤老化等因素对硒生物有效性的影响,旨在为富硒土地资源的开发利用提供科学依据。

1　土壤硒的生物有效性表征方法

土壤中硒的化学行为(图 1)复杂多样,涉及吸

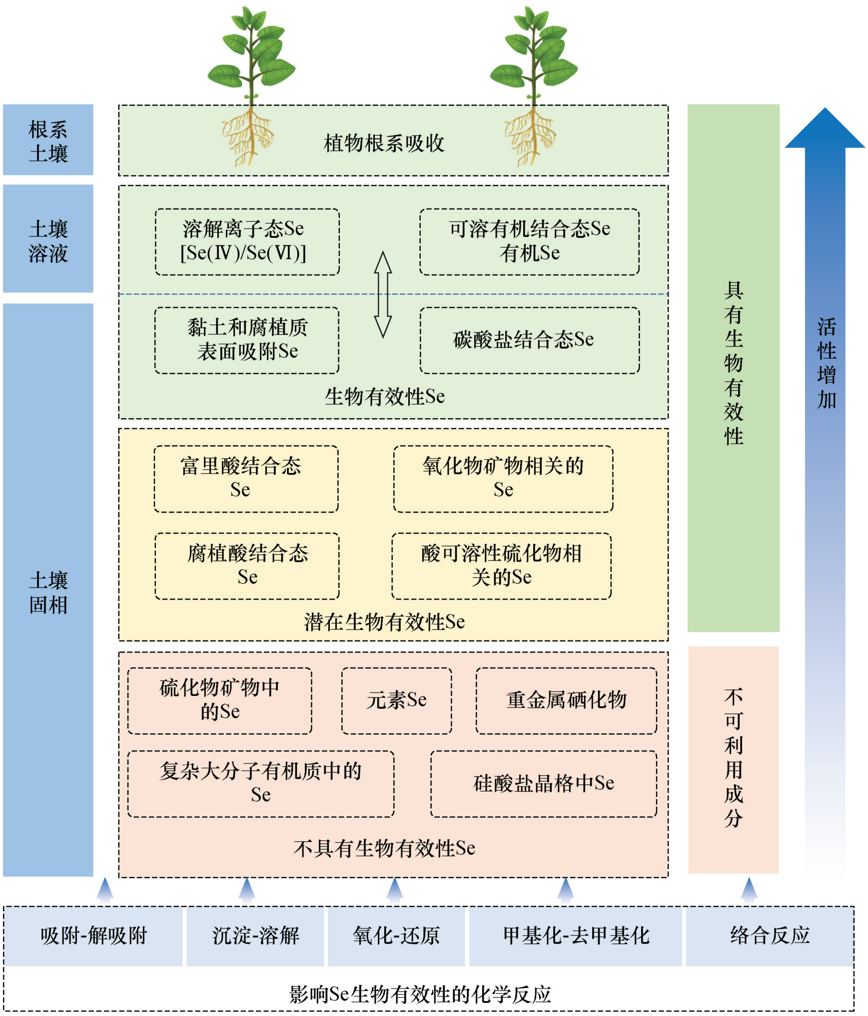

图 1　土壤-植物系统中硒的生物有效性和相关的化学反应(据 Dinh 等[15]修改)

Fig. 1　The bioavailability and associated chemical reactions of selenium in soil-plant systems (The grey-blue parts on the left side presents, from top to bottom, the root soil, the soil solution and the soil solid phase; the blue arrow on the right side indicates the increase in bioavailability of selenium from bottom to top). Modified from Dinh, et al[15].

附-解吸附、沉淀-溶解、氧化-还原、甲基化-去甲基化以及络合反应等过程,每种反应都会影响硒的生物有效性,且受到土壤 pH、土壤有机质、金属氧化物、黏土和微生物等因素的影响和制约[19-22]。根系是大部分植物吸收硒的部位,然后进行体内的转运、代谢和积累。植物根系直接吸收的硒,如土壤溶液中以游离离子形式存在的硒、碳酸盐结合态硒、黏土和腐植质表面吸附的硒等,但亚硒酸盐和硒酸盐可在局部缺氧区(如土壤团聚体)中或被细菌用作终端电子受体时还原为不具有生物有效性的固态、不溶性 Se(0)和金属-Se 沉淀物(如 FeSe、$FeSe_2$)[23];进入矿物晶格的硒和腐植质结合的硒同样不具有生物有效性。也有一部分土壤硒具有潜在生物有效性,它们通过从不稳定的或可逆的部分池中释放出来或与植物根系的接触而在特定时间被利用。如在还原条件下,铁锰氧化物结合态硒和可溶性有机质黄腐酸结合硒沉淀发生溶解,释放可溶性硒,从而大大提高了其生物有效性。

自然条件下对土壤硒的生物有效性的影响是复杂多样的,需通过研究表征方法及影响因素来综合判断土壤中硒活性。因此,如何准确地判断土壤中硒的存在形态、评估其生物有效性具有重要实际意义,且面临一定的挑战。目前表征土壤硒生物有效性的方法主要有传统的化学提取法(单一提取和顺序提取)和新兴的梯度扩散薄膜技术(DGT),各有优点和局限。

1.1　传统的化学提取法

单一提取是传统的化学提取法之一,它使用不同的单种化学提取剂一步提取对应形态的硒:水或盐溶液可提取可溶性硒组分[24];磷酸盐缓冲液可提取可溶性硒和交换性硒[25];氟化铵能够从氧化铝表面提取硒[26];浓盐酸可提取氧化结合态硒,稀释的氢氧化钠和过氧化氢溶液均可提取有机硒化物,与铁锰氧化物、硫化物和钙的化合物等结合的难溶态硒可以用强酸(硝酸)或氧化剂溶解[27];络合提取剂乙二胺四乙酸(EDTA)和二乙烯三胺五乙酸(DTPA)可提取铁锰氧化物结合态、有机结合态硒[28]。研究土壤硒的生物有效性时,单一提取法往往需要使用两种或两种以上的化学提取剂以及根据土壤性质配制不同的固液比的提取剂,如酸性土壤适宜用 0.1mol/L 的磷酸氢钾提取,富含有机质的土壤使用稀释的氢氧化钠或次氯酸钠的提取效果更好[29];也有研究表明,络合提取剂或酸性提取剂(如 0.1mol/L 盐酸)提取测定元素的浓度与植物吸收之间的相关性较差[30];且操作略微繁琐,一些提取剂的提取成分存在重合,存在确定的硒形态测定结果并不精确的问题。

顺序提取法比单一提取法能更全面地检测土壤中不同形态的硒含量。目前常用的是五步提取法,通过每一步添加不同的提取剂,及时提取出相应的组分,减小了对后续步骤中提取其余组分的影响。实验步骤一般是按照可溶性硒—交换性硒—铁锰氧化结合态硒—有机结合态硒—残余态硒的顺序进行提取,土壤中硒的溶解度和生物有效性随着提取步骤的增加而逐渐降低[31]。Peng 等[32]通过连续提取确定土壤中硒的组分,结果表明可溶性硒是评价土壤中硒酸盐的硒生物有效性的合适指标,交换性硒更适合表达土壤中亚硒酸盐的硒生物有效性。Ali 等[33]也证明了类似的结果,亚硒酸盐处理的土壤硒的有效性略低于硒酸盐处理的土壤。但是顺序提取法也存在一定的局限性,如再吸收、提取不完全情况,以及提取过程中可能因使用的化学品而改变硒的形态[34],多次的洗涤步骤可能会导致硒浓度的稀释,一系列的摇动、离心和过滤过程也会增加硒流失、污染以及硒再吸收的风险[24]。通过控制操作过程中连续提取前几个步骤的提取时间或固相与提取试剂的接触时间,可减少再吸附发生的几率[35]。

1.2　新兴的梯度扩散薄膜技术

土壤理化性质以及采样、提取、分析过程中人工操作差异,可能会影响单一提取法对土壤硒生物有效性的表达,且植物对硒的吸收是一个动态过程,单一提取和连续提取的结果不能完全反映土壤硒的动态迁移[36],因此我们需要能测量土壤溶液中的元素和从固相补充的元素,并对土壤元素释放动力学作出反应的方法。

梯度扩散薄膜技术(DGT)可模拟植物的吸收过程,被广泛应用于土壤和沉积物中重金属离子(如铅、镉、铜、锌、镍、砷等)和阴离子的测定[37]。大量研究表明,DGT 法比单一提取法和顺序提取法更能反映土壤元素的生物有效性。DGT 能反映动态系统的供应情况,模拟跨植物细胞膜的吸收过程,因此 Zhang 等[38]认为,DGT 是将实验室试验和现场观测数据进行规范化和比较的有效工具。Wang 等[39]对比了不同方法测量土壤硒生物有效性的可靠性,其顺序为:DGT>土壤溶液>顺序提取>氯化钾>热水>碳酸氢钠>EDTA>DTPA>氢氧化钠。Peng 等[40]使用亚硒酸盐和硒酸盐处理盆栽土壤,表明 DGT 是预测植物对硒酸盐吸收的一种可行方法,但不能预测亚硒酸盐的吸收。外源磷、硫易被土壤吸附,从而可以取代固定位点的硒,硒从相对稳定的状

态转化为可溶态和不稳定状态而被植物吸收,提高硒的生物有效性。这一观点也得到了 Jiang 等[41]的支持,通过施磷硫肥使小白菜根、地上部分硒含量增加 340%~360%,植物根系吸收组分显著提高,但过量施肥有抑制作用。虽然 DGT 考虑了土壤孔隙水中营养元素和土壤固液相之间元素的动态供应,相比传统的化学形态具有更好的预测性,但 Nowack 等[42]认为土壤再补给动力学室内模拟实验与野外原位土壤样品仍然存在差异,因此实验室模拟实验还不能充分预测野外原位土壤样品。

表 1 总结了采用传统提取法和 DGT 法对土壤生物有效性进行评价的案例。按照不同地区土壤中的提取分析结果,可以看出化学形态单一提取法获得的组分简单,不一定能代表其生物有效性;顺序提取法则全面分析了硒的存在形态,与作物硒具有一定的对应性;DGT 提取的硒与作物硒的相关性更为密切。

1.3　区域尺度硒生物有效性评价方法

近些年来,研究者通过定义一些参数来直观地反映评价硒的生物有效性,如迁移因子 MF(Mobility Factor)可以表征硒的相对迁移指数,MF 越高,硒可被植物吸收的程度越高,硒生物有效性越高[54];

表 1　土壤硒生物有效性评价研究案例

Table 1　Cases of soil selenium bioavailability assessment

评估方法	土壤类型	地区	作物	影响硒生物有效性因素	参考文献
单一提取法	草甸黏壤土	英国	-	可溶性硒、交换性硒为主要的有效硒组分	[24]
	黄褐色土	湖北省恩施市	马铃薯	硒酸盐比亚硒酸盐更能提高块茎硒的生物有效性,但膨大期叶面施用亚硒酸盐适合富硒马铃薯的生产	[43]
	水田土,旱地土	湖北省恩施市	水稻	水稻植株的硒含量与有机结合态硒呈显著相关,有机质是影响水稻硒生物有效性的主要因素	[44]
	黄土,砂壤土	陕西省永寿县	玉米	土壤和叶面施加硒均能可靠有效地提高玉米籽粒中硒的含量	[45]
	变性土,铁铝土	云南省滇池东岸	-	土壤中的总硒含量对生物有效性硒影响最大,其次是铁/铝氧化物,pH 增加时铁/铝氧化物对硒的吸附降低	[46]
	富硒土壤,风化石煤	湖北省恩施市渔塘坝	-	弱结合的腐植酸结合态硒在有机结合态硒中占主导地位,且结合越弱越容易转化成生物有效性硒,是生物有效性硒的潜在来源	[47]
	泥炭土、壤土,泥炭/壤土混合土	挪威东南部	小麦	有机质含量较低的土壤,硒有效性随 pH 的增加而增加;有机质含量较高的泥炭土,硒有效性随 pH 的增加而降低	[48]
顺序提取法	水稻土,旱地土	陕西省紫阳县闹热村	水稻,玉米	旱地中铁锰氧化结合态硒占主导地位,有机结合态释放硒会提高硒的生物有效性	[25]
	黄土	陕西省	小白菜	硒酸盐比亚硒酸盐处理的土壤有更高的生物有效性	[32]
	黄土,壤土	西北农林科技大学试验田	小麦	亚硒酸盐处理,交换性硒浓度增加;硒酸盐处理,可溶性硒浓度增加;铁锰氧化结合态硒、有机结合态硒浓度均降低;硒生物有效性增加	[33]
	大骨节病病区的天然土壤	西藏高原松潘县	青稞	硒的生物有效性与海拔高度呈负相关	[49]
	栗钙土,黑土	内蒙古和黑龙江	小白菜	老化使可溶性硒和交换性硒随时间延长而含量降低,硒生物有效性降低	[50]
DGT 技术	天然富硒土壤	湖北省恩施市	水稻	DGT 测定的硒主要来源于可溶性和可交换态硒,可溶性和交换性硒浓度与土壤 pH 呈显著正相关	[36]
	天然富硒土壤	陕西省紫阳县	玉米	残余态硒和铁锰氧化物结合态硒占据优势,交换性硒和碳酸盐结合态硒占比<5%,生物有效性很低	[39]
	农场表层土	西北农林科技大学农场	紫甘蓝,西兰花,芥菜,小麦	紫甘蓝和西兰花吸收土壤中最有效的可溶性硒的能力优于芥菜和小麦,DGT 适用于表征硒酸盐处理的土壤硒生物有效性	[40]
	栗钙土,黑土	内蒙古和黑龙江	小白菜	小白菜根中硒浓度与 C_{DGT-Se} 呈极显著相关,硒酸盐处理的土壤老化速率低于亚硒酸盐处理的土壤,老化使硒生物有效性均降低	[51]
	水培溶液	-	油菜,小麦	油菜对硒的积累速度大约是小麦的三倍	[52]
	黄棕壤、砂姜黑土、褐土、海滨土、黑土和潮土	安徽、江苏、辽宁、天津、黑龙江、河北	小白菜	生物有效性:褐土>潮土,黑土>海滨土,砂姜黑土>黄棕壤,土壤类型是影响有效硒的主要因素	[53]

生物积累因子 BAF(Bioaccumulation Factor)反映植物对土壤中硒等元素的吸收和积累能力[55]。因此,可以在区域尺度建立 Se 元素在土壤-植物系统的回归方程,即通过模型搭建研究区土壤理化性质、土壤总硒、有机质和重金属等影响因素与硒的生物有效性之间关系的桥梁,预测作物籽实硒含量,从区域尺度评价硒生物有效性。

MF 可表示为:

$$MF=(F_1+F_2)/(F_1+F_2+F_3+F_4+F_5) \quad (1)$$

式中:F_1 和 F_2 分别为可溶性硒及交换性硒的含量;F_1 至 F_5 为土壤中硒各形态含量之和。

BAF 可表示为:

$$BAF=C_{Se作物}/\ C_{Se土壤} \quad (2)$$

式中:$C_{Se作物}$为作物中 Se 元素含量(mg/kg);$C_{Se土壤}$为土壤中 Se 元素含量(mg/kg)。

Gu 等[56]建立了基于表层土壤性质、重金属和硒含量的 BAF 预测模型,估算了广西来宾市范围内水稻籽粒中的重金属和硒含量。Yu 等[57]建立了玉米籽实吸收土壤 Se 元素 BAF 模型,且应用基准剂量法进行了推荐限值评估,在湖北恩施研究区开展了区域尺度的硒生物有效性与富硒土地安全利用评价,在保障生态安全的前提下,在富硒土地资源分布区域内,按照农作物中硒与重金属元素含量,划分出可以安全利用开发富硒土地资源的区域。农作物中 Se 含量的分布趋势与土壤中总 Se 含量的分布趋势不同,但与土壤生物可利用 Se 含量的分布趋势一致。冗余分析(RDA)表明,土壤 pH 值和有机质是陕西小麦产区土壤 Se 生物利用率的主导影响因素,土壤 Se 生物利用率随着这两个参数的提高而上升。Liu 等[9]以此为基础,采用 MF 指数建立了模型,预测了陕西省的小麦主产区小麦籽粒中的 Se 含量。Wang 等[58]为了研究中国不同土壤老化过程中硒酸盐的再分配及其主要影响因素,进行了逐步多元线性回归分析,并建立有效硒与主要影响因素的关系模型。研究表明,土壤硒有效性主要受 pH、非晶态铁/铝、有机质和培养时间的控制,其中土壤 pH 值贡献率约占 70%。Gashu 等[59]依据农作物和土壤采样数据,建立了谷物中 Se 浓度的预测模型,并进行了交叉验证,在埃塞俄比亚阿姆哈拉地区实现了区域尺度农作物中 Se 含量预测,研究表明该区域谷物提供足够的膳食摄入硒。这些方法将预测值与实测值交叉验证,准确性较高,拓展了硒生物有效性评价的思路。

2　影响土壤硒生物有效性的因素

影响土壤硒的生物有效性,不仅包括土壤的内部因素,如地形、土壤类型、pH 和有机质,还有硒的存在形态、植物种类和老化等外部因素。综合分析认为,地形和土壤类型、硒的存在形态、土壤 pH 和有机质是影响有效硒的主要因素,植物种类和老化为次要因素。研究硒的生物有效性时,需将主要因素与次要因素统筹进行考虑。

2.1　地形和土壤类型

地形如海拔、坡度和地形湿润指数等是影响土壤有效硒含量的重要因素,导致不同地区土壤有效硒差距很大。Xu 等[60]对浙江省永嘉县土壤硒研究结果表明,随着海拔、坡度和地形湿润指数的增加,土壤全硒表现出先升高后降低的态势,磷酸盐提取的有效硒随着海拔的升高而升高,在坡度和地形湿润指数方面呈现与全硒相同的趋势。然而,Chopra 等[55]的研究表明随着海拔高度的增加,青藏高原东北缘松潘县 2200~3500m 海拔范围内的耕地表层土壤有效硒含量显著降低($r=-0.80, P=0.01$)。虽然硒的生物有效性与海拔之间的关系在不同地区存在差异,但地形地貌在一定程度上影响土壤中硒的分布和生物有效性。

不同类型的土壤其理化性质如有机质、铁/铝氢氧化物和 pH 等存在较大的差异,控制硒的迁移,影响硒的流动性,如酸性的森林土壤可形成较不稳定的有机-矿物组合,影响硒的迁移和生物有效性[61];火山土表现为总硒含量高而生物有效性低,原因是火山土富含高比表面积和正电荷以及结晶性较差的铁氧化物,如铁腐植质复合体和铁水合石,它们都对硒有高亲和力,控制了硒的迁移[62]。不同类型土壤影响硒生物有效性的原因主要有三点:①土壤酸性且富含有机质时,硒主要以迁移能力低的硒化物和硒-硫化物存在,生物有效性较低;②接近中性的矿质土中易被铁/铝氢氧化物固定的亚硒酸盐占优势,尽管碱性金属硒化物可溶,但亚硒酸铁不溶,降低了硒的生物有效性;③碱性且氧化性的土壤硒的生物有效性好。Peng 等[53]发现黄棕壤比其他土壤更容易吸附和固定硒,导致硒的生物有效性最低,潮土和海滨盐渍土是高 pH 和高碳酸盐含量的碱性土壤,其硒的生物有效性高于其他类型的土壤。发生大骨节病病区的土壤硒含量和非病区的土壤硒含量不一定存在着明显的差别,但其硒的生物有效性有着明显不同。Wang 等[63]认为原因是大骨节病病区的硒不能有效地被植物根系吸收,土壤中可溶性、交换性

和黄腐酸结合态硒与根系吸收的硒具有显著的正相关性,是迁移过程中的主要组成部分。

2.2　硒的存在形态

采用顺序提取方案,可以将土壤硒形态分为可溶性硒、交换性硒、铁锰氧化结合态硒、有机结合态硒以及低迁移率的残余态硒。可溶性硒和交换性硒被认为是高度流动或有效的,铁锰氧化物和有机质固定硒,限制了硒的迁移,但在还原条件下能释放一部分硒而具有潜在生物有效性,残余态硒是最稳定和最不活跃的硒组分[64]。

无机价态的硒在土壤中具有生物有效性的存在形态主要为硒酸盐和亚硒酸盐,还可能有零价等其他价态硒,生物有效性在很大程度上取决于土壤的湿度和酸碱性。亚硒酸盐能够在金属氧化物表面或土壤有机质表面形成强结合配合物,导致硒生物有效性降低;而硒酸盐被外球表面络合物的静电力弱吸附而更易交换,易通过径流从土壤中淋滤,有很好的流动性,被植物体吸收、转运和代谢更容易,相对于亚硒酸盐供应下的硒主要在植物根部积累,硒酸盐处理下的硒更多转运到叶片,其生物有效性更好[65]。Longchamp 等[66]对成熟玉米中硒的吸收、积累、分配和代谢进行了研究,结果表明硒酸盐处理后的植株中顶部硒含量为总硒的 90%以上,叶片硒含量约 50%;而亚硒酸盐处理的植株顶部仅有 40%的硒含量,根部约为 60%,籽粒硒含量不受影响,两种无机硒处理下均占植物硒总量的 15%,说明作物硒的吸收、积累、分配和代谢取决于硒的供给形式。

植物硒被人或动物摄入后进入体循环的是生物有效性硒。有研究表明,主要来自植物和动物的有机形式(例如半蛋氨酸和半胱氨酸)比主要在膳食矿物质补充剂中发现的无机形式(硒酸盐和亚硒酸盐)有更多的生物利用度[67],即有机硒是最有生物有效性的硒的存在形态。Supriatin 等[68]通过次氯酸钠氧化萃取法测得的有机硒平均占总硒的 82%,表明荷兰农田土壤中的大部分硒以有机形式存在。Thiry 等[69]认为从长期来看,以硒蛋氨酸形式存在的有机硒更能有效地预防硒缺乏,而亚硒酸盐形式存在的无机硒可以对硒的急性需求作出更快的反应,但从长期来看,具有更高的毒性风险。

2.3　土壤 pH

pH 主要通过控制氧化还原过程、调节吸附/解吸和沉淀/溶解过程来影响硒的形态和迁移,从而对硒的生物有效性产生影响,影响机制见图 2。

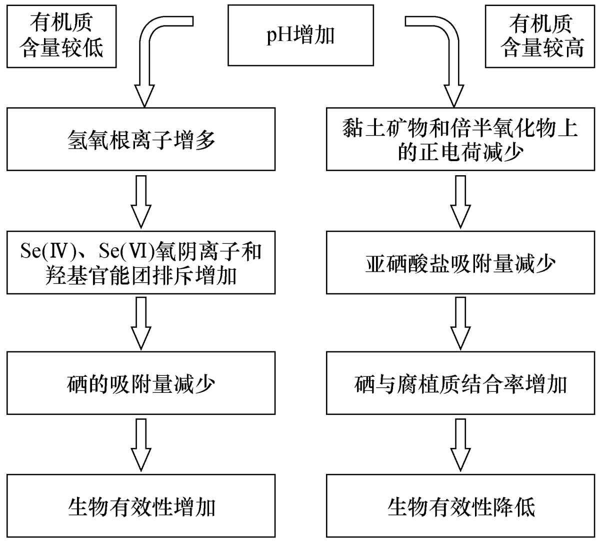

图 2　土壤 pH 对硒生物有效性的影响

Fig. 2　The impact of soil pH on selenium bioavailability.

Se(Ⅵ)主要存在于碱性和氧化条件下,有着很高的流动性和溶解度,根系吸收比较容易;Se(Ⅳ)随着 pH 的降低占据主要地位,易被土壤固相吸附和固定[35];Se(0)和 Se(Ⅱ)存在于强还原条件下,负价的硒和土壤中增多的正电荷形成吸附并固定,生物有效性大大降低。由于土壤 pH 增加,氢氧根离子数目增加,造成土壤表面 Se(Ⅳ)或 Se(Ⅵ)氧阴离子和羟基官能团之间产生静电排斥,土壤对硒的吸附量降低,从而增加了硒的生物有效性[70]。He 等[71]报道了在酸性条件下,亚硒酸铁可以在土壤和沉积物中形成难溶性沉淀物。陈继平等[72]对比分析了酸性土壤和偏碱性土壤中小麦根系土与籽粒中硒含量和硒形态,数据表明在弱碱性和碱性土壤中种植的小麦的富硒率明显高于酸性土壤。

然而,提高 pH 并非在任何情况下都能提高硒的生物有效性。Tsioubri 等[73]发现,对生长在酸性和有机质含量较高的碱性土壤上的莴苣和三叶草施硒可提高植物硒含量,但 pH 对硒吸收的影响随土壤有机质含量的增加而减小,表明对于富含有机质的土壤提高 pH 不是提高硒生物有效性的合理措施。对此可解释为:土壤有机质水平较高时,pH 增加使黏土矿物和倍半氧化物上的正电荷数目减少,与之结合的亚硒酸盐吸附量减少;尽管在一般情况下,阴离子主要结合于矿物表面,只有少量与有机质结合,但由于微生物活性增加,由微生物介导的硒阴离子还原到低价态的概率增大,使得更多的硒与腐植酸结合,土壤硒的生物有效性变化呈现出相反的情况[48]。

2.4　土壤有机质

土壤有机质(SOM)对土壤硒的生物有效性具有双重调节作用,通过形成有机质结合的硒缔合物或从有机质结合的硒复合体中释放硒,即它能在铁、铝氧化物存在下形成三元配合物固定硒,并促进形成缺氧区(如土壤大团聚体的核心),从而促进硒的减少和固定[74];与有机物结合的硒也能矿化为无机硒和易于被植物吸收的小型有机硒化合物[75],形成土壤硒生物有效性的动态平衡,受到物理、化学、生物过程和驱动因素影响(图 3)。Tolu 等[23]研究结果表明对于有机质含量小于 20%的土壤,土壤硒的溶解度主要取决于其对结晶氢氧化物的吸附。Li 等[74]报道认为与土壤有机质相关的硒可以缓慢释放并补充土壤溶液中的硒,有机结合态硒可以作为土壤中生物有效态硒的潜在来源。

有机酸是土壤有机质中最重要的活性成分,包括低分子量有机酸和高分子量有机酸。Adeleke 等[76]发现,一些低分子量有机酸可以通过改变土壤 pH 值来溶解不溶性矿物,将硒释放到土壤溶液中。Martin 等[77]发现硒可与 Fe(Ⅲ)和腐植酸(HA)结合,形成 Se-Fe-HA 三元络合物并沉淀。影响硒生物有效性的情况如图 4 所示:低分子量有机酸可通过竞争吸附位点来提高硒的迁移率或改变 pH 溶解不溶性矿物释放硒;与之相反的是,高分子量有机酸中腐植酸占主导时降低硒的迁移率[36]。黄腐酸(FA)和腐植酸(HA)是高分子量有机酸的主要组分,与黄腐酸结合的硒可被分解并易于被植物利用,而与腐植酸结合的硒稳定且难以分解,导致生物利用度低[56]。Qin 等[47]得到在所有富硒土壤和风化石煤样品中,FA-Se 是主要存在形式,占有机质结合硒(OM-Se)的 62%以上,并且认为弱结合的 FA-Se 可能是 OM-Se 中生物有效硒的潜在来源,而强结合的 HA-Se 可能是 OM-Se 中的生物有效硒汇。这一观点也得到了 Wang 等[78]研究结果的支持,他们发现富硒土壤老化一年之后,土壤溶液、颗粒表面和固相中的 FA-Se 与土壤有效硒显著相关。

2.5　植物种类

人类每日摄入的硒中,近 85%直接或间接来源于植物。植物能通过硫转运体和生化途径吸收和同化硒,也易挥发甲基化的硒,因此植物既可为缺硒地区提供膳食硒,又可消除含硒地区的硒污染[79]。非硒积累型植物的硒含量低于 100mg/kg(干重),硒指示植物的硒含量可达 100~1000mg/kg(干重)且无毒性迹象,硒超积累植物的硒积累量超过 1000 mg/kg(干重)[80]。例如,黄芪属植物中绝大多数是硒超积累植物[81],小白菜属芸苔科,具有较高的硒积累能力,可作为富硒植物进行开发利用[82]。很多研究已经证明了不同种类的植物对硒的积累能力存在显著差异,同一作物在不同的生长阶段对硒的吸收量有高低之别[83-86]。

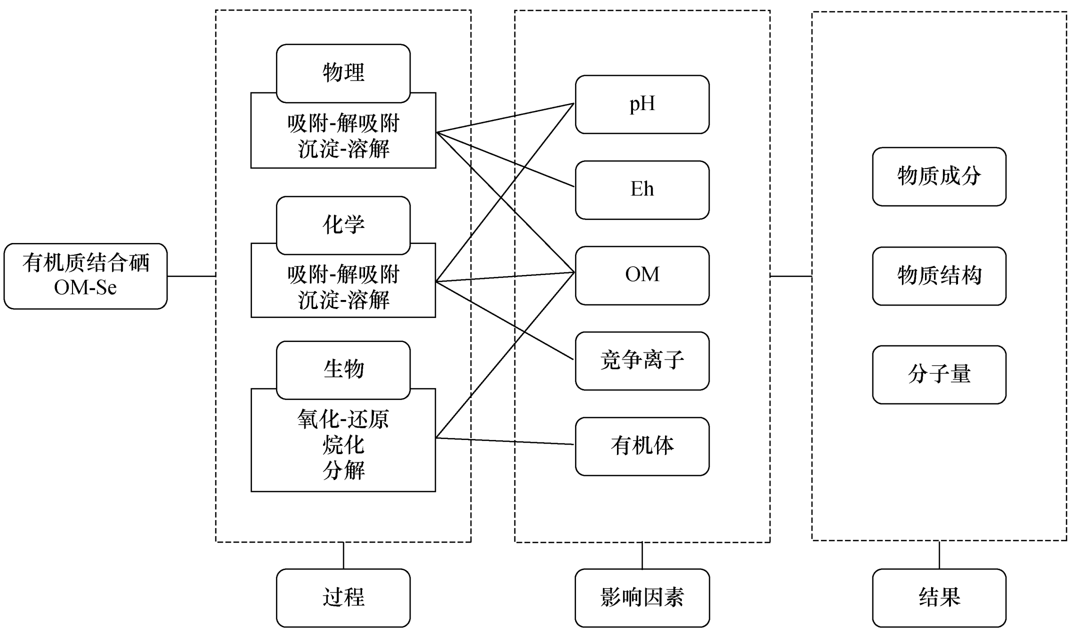

图 3　土壤中有机质对硒的影响及相关驱动因素(据 Li 等[74]修改)

Fig. 3　The impact of soil organic matter on selenium and associated driving factors (Modified from Li, et al [74]).

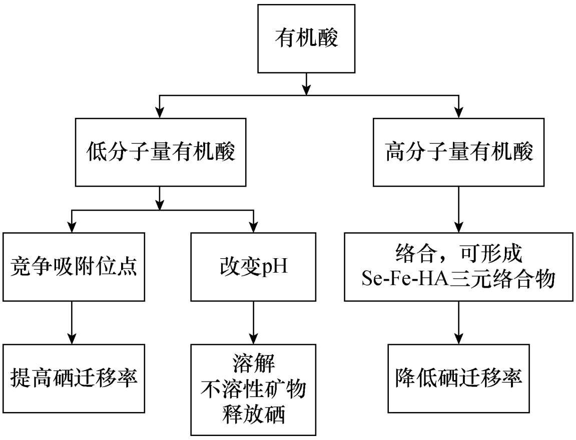

图 4　有机酸对土壤硒生物有效性的影响示意图

Fig. 4　The impact of organic acids on soil selenium bioavailability.

土壤硒的生物有效性影响植物体内的硒含量，同样植物也会反作用于土壤，硒超积累植物对周围土壤中硒有富集作用，影响硒的生物有效性[87]。土壤的有机态硒是生物有效硒的主要来源，通过植物的分解产物及合成物形成，硒超积累植物的枯落物和作物根系释放的化合物富集根系土壤的硒，并通过产生影响根际生物的分泌物调动土壤中不稳定的硒，增加周围土壤硒的生物有效性，El Mehdawi[88]通过研究硒超积累植物间的相互作用证明了这点；另一方面，由于植物根系释放有机化合物、酶以及降解有机物质的质子影响根际化学，进而影响土壤溶液中硒的存在形式，这与生物有效性硒直接相关[79]。且植物凋落物、根系分泌物和土壤腐植质可形成土壤溶解性有机物，相比土壤中的固相有机质有更好的溶解性和更多的结合位点，影响硒的溶解度，这也可能是硒超积累植物影响硒生物有效性的重要原因[89]。

2.6　土壤老化

老化是指外源化学物质在土壤中的流动性、生物有效性或毒性随时间而下降的过程[51]。当外源硒酸盐进入土壤后，随着时间的延长，硒酸盐从可溶性（中性或碱性土壤）或交换性（酸性土壤）组分向铁锰氧化结合态、有机质结合态和残留态转化，硒的有效性降低。老化速率和时间随土壤性质（pH、非晶态铁/铝和有机质）的变化而变化：碱性条件下 Se(Ⅵ)缓慢还原为 Se(Ⅳ)并吸附于碳酸盐、铁锰氧化物和有机质上；酸性条件下亚硒酸盐被迅速还原，固定在铁锰氧化物上或与有机质结合，酸性土壤的老化速率大于碱性和中性土壤[90]。

如图 5 所示，一般认为老化机理主要为微孔扩散，表面成核/沉淀和有机质固定，对应老化的五个过程：①外源硒扩散到土壤中的矿物或有机物表面的微孔中；②吸附在矿物表面的硒逐渐扩散到矿物晶体中；③以离子形式存在的硒与土壤形成新的固相；④硒的沉淀或氧化/还原过程；⑤硒通过扩散更紧密地结合在有机分子中[91]。老化过程中具有大表面积、微孔结构和丰富结合位点的铁、铝和锰的非晶态氧化物以离散相的形式出现或作为其他矿物表面的涂层，与表面成核/沉淀老化机制或吸附行为密切相关，且吸附能力随 pH 的降低而增加，影响硒的迁移和生物有效性[92]。Tolu 等[93]研究了硒输入后短期和长期土壤中硒的迁移和组分，表明随着培养时间的延长，土壤中可溶性硒和交换性硒含量降低，有机结合态硒含量增加。此外，老化也受到土壤水分的影响，水饱和时土壤 Eh 降低，高价态硒还原为低价态，可溶性硒含量迅速下降，土壤老化速率加快[94]。

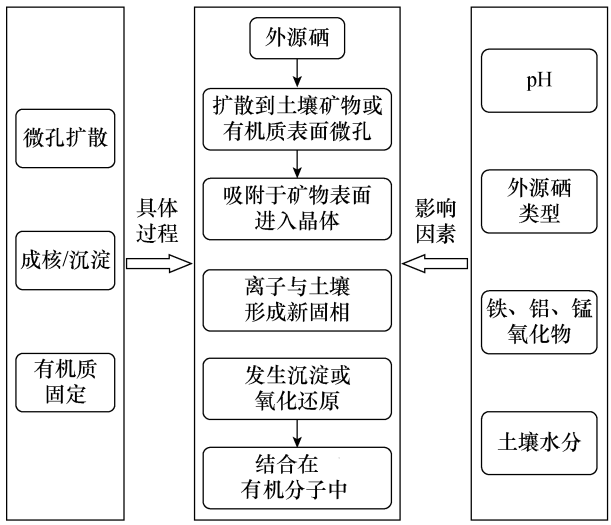

图 5　土壤老化过程及影响因素

Fig. 5　Soil ageing process and influential factors.

3　结语与展望

对于不同硒的生物有效性的表征方法，主要局限性为：单一提取法会被土壤性质、土壤/溶液比、提取时间和提取剂的 pH 值等影响提取效果；顺序提取法存在提取不完全，洗涤稀释浓度以及离心过滤过程中硒流失的问题，且这两种传统的提取方法均不能反映固相-土壤溶液-根部系统的动力学过程。薄膜扩散提取技术恰好是一种扰乱土壤溶液和固相

之间的平衡，模拟根系吸收硒的动态过程，在评估有效性方面更具优势，但对于是否能够充分地预测野外土壤的再补给动力学有待商榷。

影响土壤硒生物有效性的主要因素：①地形因素如海拔、坡度和地形湿润指数等对土壤硒含量有一定的影响，不同类型土壤的有机质、铁/铝氢氧化物和 pH 等存在较大的差异，通过控制硒迁移影响硒的生物有效性；②可溶性硒和交换性硒更易被植物吸收，流动性更好的硒酸盐相比亚硒酸盐在植物体的吸收、转运和代谢方面更容易；③通常情况下增加土壤的 pH 能够提高硒的生物有效性，但富含有机质的土壤则相反。

目前受地形、土壤类型、土壤理化性质等诸多因素影响，对于土壤硒生物有效性的评价并没有一个普遍且广泛适用的方法，导致不同结果间难以相互比较和验证。完善 DGT 原位分析技术和改进元素形态分析测试技术，是准确评价土壤硒生物有效性的重要技术手段，也是未来发展的重要方向。

A Summary of Research Progress on Bioavailability Assessment Method of Selenium in Soil and Its Influencing Factors

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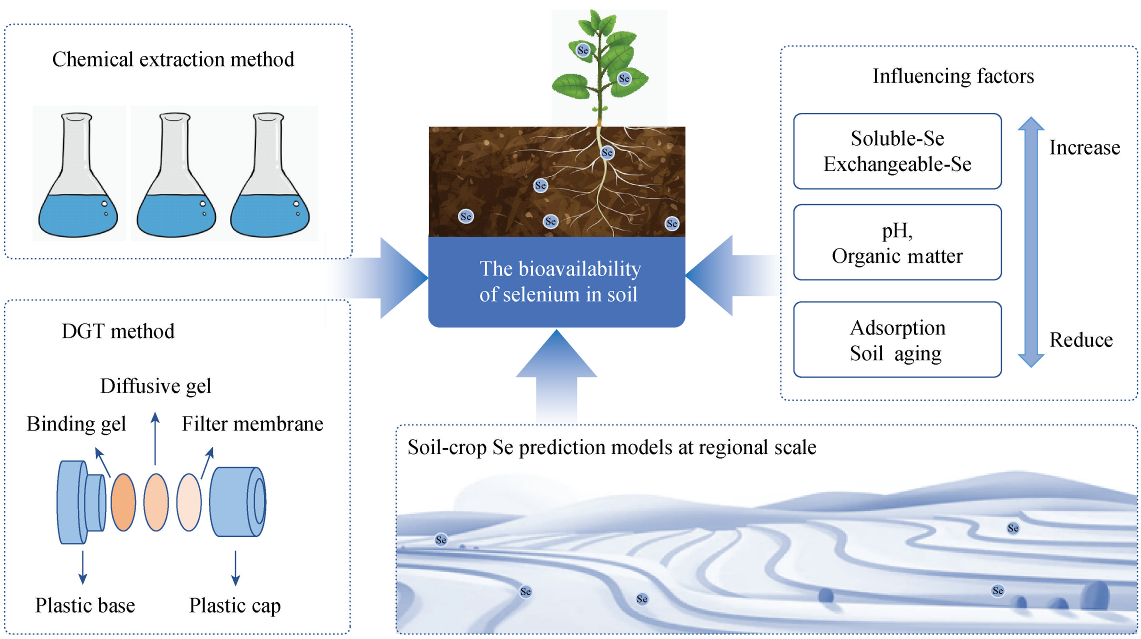
HIGHLIGHTS

(1) The chemical extraction method and DGT technology are limited in accessing the bioavailability of soil selenium.

(2) The soil selenium bioavailability assessment models are acceptable at the regional scale prediction.

(3) Soil parent materials and soil physicochemical properties play a significant role in determining the uptake of soil selenium by plants.



ABSTRACT

Selenium (Se) is a trace element that plays a crucial role in human health. It has antioxidant, anti-cancer and anti-viral properties and is essential for a healthy body. The level of Se in the human body is largely dependent on daily dietary intake, which is in turn influenced by the amount of Se that enters the food chain from the soil. The global distribution of Se in soil is uneven, with a large difference in concentrations ranging mainly between 0.01-2.0mg/kg. The average abundance of Se in the Earth's crust is 0.07mg/kg, but in some Se-enriched areas, it can reach up to 1200mg/kg. The chemical behavior of Se in soils is complex and diverse, involving processes such as adsorption - desorption, precipitation - dissolution, oxidation - reduction, methylation - demethylation and complexation reactions, each of which affects the bioavailable Se and is influenced and conditioned by factors such as soil pH, soil organic matter, metal oxides, clay and microorganisms. Roots are the primary site for most plants to absorb Se, which is then transported, metabolized, and accumulated. Plants can directly absorb Se from the soil, including Se that exists in the form of free ions, carbonate-bound Se, and Se adsorbed on the surfaces of clay and humus in soil solutions. However, selenite and selenate can be reduced to solid, insoluble Se(0) and metal-Se precipitates that are not bioavailable in locally anaerobic areas (such as soil aggregates) or used by bacteria as terminal electron acceptors.

Previous researchers have conducted a lot of work on chemical extraction methods, but there are still problems, such as insufficient extraction specificity and Se form transformation during the extraction process. Hence, an accurate approach for predicting the amount of soil Se that can be absorbed by plants is essential. However there are no clear paths for the choices of assessment methods and influencing factors of soil Se bioavailability. These problems have restricted the utilization of Se-enriched land resources. Thus, providing a scientific basis for the development and utilization of Se-enriched land resources is the goal here by summarizing the main assessment methods and dominant factors on soil Se bioavailability.

Determining the activity of Se in soils comprehensively requires considering the complicated and varied effects of natural conditions on its bioavailability, which can be studied through characterization methods and identification of influencing factors. Therefore, it is of practical importance and a challenge to accurately determine the form of Se in soils and assess its bioavailability. Current methods for characterizing the bioavailability of soil Se include the traditional chemical extraction methods (single extraction and sequential extraction) and the emerging Diffusive Gradients in Thin films (DGT) technique. Chemical extraction is a process that involves separating a specific component or substance from a mixture using a solvent or a chemical reagent. The extraction method depends on the physical and chemical properties of the substance being extracted and the nature of the mixture. The general steps involved in a chemical extraction method are: choosing the appropriate solvent or chemical reagent that can selectively dissolve the desired substance while leaving the unwanted components behind, mixing the mixture and the solvent/reagent together to allow the selective extraction of the desired substance, separating the extracted substance from the mixture using various techniques such as filtration, centrifugation, or evaporation, and purifying and isolating the extracted substance by further chemical or physical methods if necessary. The DGT technique is an effective environmental chemistry method used for identifying elements and compounds in various aqueous environments, including natural waters, sediments, and soils. This technique is particularly useful for detecting bioavailable trace elements, and it can be applied for *in-situ* detection. The DGT technique involves using a specially-designed passive sampler that comprises a binding gel, a diffusive gel, and a membrane filter. The element or compound of interest passes through the membrane filter and diffusive gel before being assimilated by the binding gel in a rate-controlled manner. Subsequently, the binding gel is analyzed post-deployment, enabling the determination of the time-weighted-average bulk solution concentration of the element or compound via a simple equation.

The advantages and limitations of chemical extraction methods, DGT technique and bioavailability assessment models of Se at a regional scale are compared. Traditional chemical extraction procedures such as single extraction or sequential extraction can be used to characterize the bioavailability of Se in the soil, to a certain extent. Still, the extraction process has many limits and incomplete extraction problems. The DGT method can be used to simulate the root uptake process of plants and can better characterize the bioavailability of Se compared to sequential extraction. One of the major advantages of the DGT technique is its ability to provide accurate and reliable results, even at low concentrations. Additionally, this technique is non-destructive and can be used *in-situ*, making it suitable for real-time monitoring of environmental conditions. However, there are also some limitations associated with the DGT technique. For instance, the binding gel used in this method may not be specific to the target element or compound, leading to the possibility of cross-reactivity with other substances. Additionally, the technique may be influenced by factors such as temperature, pH, and ionic strength, which could affect the accuracy of the results. Using large-scale crop-root soil samples, a soil-crop Se assessment model was developed with parameters of physicochemical indicators (e. g. soil pH, soil organic matter, soil Se, etc.), which can better predict Se bioavailability on a regional scale.

Some major and minor influencing factors affecting the uptake of Se in soil by plants are discussed. In short, topography and soil type, Se species, pH and organic matter are the main factors affecting bioavailable Se, with plant species and soil aging as secondary factors.

In brief, the main limitations of the characterization methods for the bioavailability of different forms of Se are: a single extraction method can be affected by soil properties, soil/solution ratio, extraction time, the pH value of the extraction agent, and other factors. Sequential extraction methods have problems with incomplete extraction, dilution of the extract, and Se loss during centrifugation and filtration. These traditional methods cannot be used to reflect the dynamic processes of the solid-phase soil-solution-root system. DGT technology is a method that disturbs the equilibrium between soil solution and solid phase, simulating the dynamic process of Se uptake by roots, and has advantages in assessing bioavailability. However, it is still questionable whether it can be used to fully predict the replenishment dynamics of Se in field soil. The main factors affecting the bioavailability of soil Se are: (1) Topographical factors such as altitude, slope, and terrain wetness index, which have some influence on soil Se content; there are large differences in organic matter, iron/aluminum hydroxides, and pH among different soil types, which can be controlled to affect Se migration and bioavailability; (2) Soluble and exchangeable Se are more easily absorbed by plants, and selenate with better mobility is easier to absorb, transport, and metabolize in plants than selenite; (3) Increasing soil pH can generally improve Se bioavailability, but this is not the case in organic-enriched soils. Currently, there is no universally applicable method for evaluating soil Se bioavailability, as it is influenced by many factors such as topography, soil type, and soil physicochemical properties. This makes it difficult to compare and verify different results. Improving *in-situ* DGT analysis technology and modifying the analysis of Se forms are important technical means for accurately evaluating soil Se bioavailability and are also important directions for future development.

KEY WORDS: selenium; soil; bioavailability; influencing factors; chemical speciation; assessment method

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