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草甘膦的水环境行为及其对水生生物毒性的研究进展

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摘要: 草甘膦是世界上应用最广泛的除草剂,在水环境中普遍存在,其环境残留可能会危害非靶标水生生物,严重威胁水生生态系统健康,因此受到人们的广泛关注。本文整理分析了水环境中草甘膦的来源、污染现状和水环境行为,详细探讨了其对水生生物的毒性效应,并且对该领域的未来发展趋势做出了简要分析与展望,旨在为草甘膦的水生生态毒性和环境风险评估提供参考依据,为合理使用草甘膦提供一定的指导作用。

关键词: 草甘膦;水环境行为;毒性效应
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Advances of Aquatic Environmental Behaviors and Toxicity of Glyphosate to Aquatic Organisms

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Abstract: Glyphosate is the most widely used herbicide in the world, and it is widespread in the aquatic environment. Glyphosate residues may harm the non-target aquatic organisms and pose serious threat to the health of aquatic ecosystem, which has been received extensive attention. In this paper, the sources, pollution status and water environmental behaviors of glyphosate are reviewed, their toxic effects to aquatic organisms are discussed and the prospects of future research are also proposed. This review would provide scientific basis for aquatic ecotoxicity and environmental risk assessment of glyphosate, which will be helpful to guide the rational use of this herbicide.

Keywords: glyphosate; aquatic environmental behaviors; toxic effect

草甘膦(glyphosate)是一种内吸传导型广谱灭生性有机磷类除草剂,具有无选择性和活性强等特点,可用于单子叶和双子叶杂草的防除[1-3]。因此,鉴于草甘膦良好的除草性,其在果园茶桑、橡胶园、农田菜地、水产养殖区、森林防火隔离带、边境防火道以及铁路机场、仓库、河道、公路绿化带、草原改良及轮作地块等化学除草中均得到广泛应用[4-5]。草甘膦的分子式为 $C_3H_8NO_5P$,纯品为白色固体,具有高度

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亲水性,溶解度为 1×10^{3} ~ 1.57×10^{4} $mg\cdot L^{-1}$,不易挥发[6−7]。草甘膦的主要存在形态为酸和盐[8],盐形式的灭草活性比酸形式的高[9],常见种类包括草甘膦铵盐、草甘膦二铵盐、草甘膦二甲胺盐和草甘膦钾盐等。目前市场上最常用的商品是农达[9],质量分数为 41% 的草甘膦水剂,由草甘膦异丙胺盐、水和表面活性剂 2-苯氧乙基丙烯酸酯(POEA)组成[10]。

草甘膦在农业除草及提高农业经济作物生产效率方面发挥着巨大作用,然而草甘膦的频繁使用可能会污染水环境,水环境中草甘膦污染物的残留可能会危害非靶标水生生物,严重威胁水生生态系统的环境安全[3]。本文在分析水环境中草甘膦的来源、污染现状及环境行为的基础上,重点阐明草甘膦对水生生物的毒性效应,并对未来研究的方向进行展望,旨在为草甘膦的水生生态毒性和环境风险评估提供参考依据,为合理使用草甘膦起到一定的指导作用。

1　水环境中草甘膦的来源和污染现状(The sources and pollution occurrence of glyphosate in the aquatic environment)

1.1　水环境中草甘膦的来源

草甘膦在农业除杂草中的应用是水环境中草甘膦的主要来源之一,其在农业喷洒施用过程中的地表径流、直接过量喷洒或漂移会导致大量草甘膦进入水环境中,大量研究表明,农业中频繁和长期使用农药会导致地下水[5, 11]和地表水环境[12−13]污染。此外,一些草甘膦合成工业或纺织工业的工业废水及城镇污水处理厂排放的废水也是水环境中草甘膦的来源之一[14−18],所排放的含草甘膦的废水最后可能进入海洋区域,特别是河口和沿岸地区[19]。水环境中残留的草甘膦不但给水环境系统带来了污染,而且可能会引起水生生物(植物、动物和微生物等)的毒性效应,其在水环境中的吸附迁移和发生目前已经引起了社会高度关注。

1.2　水环境中草甘膦污染现状

草甘膦在全球范围内推广应用已有 40 多年的历史,且使用量大居农药之首,因而可通过各种途径进入到水环境中并造成不同程度的污染。草甘膦通过喷洒,可直接进入大气环境,雨水中的浓度可高达 0.20 ~ 0.80 $mg\cdot L^{-1}$[20]。通过径流,草甘膦可在地表水和地下水以及全球沉积物中被检测到[21−23],如在德国河口海岸带海水中其浓度范围在 2.80×10^{-5} ~ 1.69×10^{-3} $mg\cdot L^{-1}$之间[24],而西太平洋海水样本中其浓度在 0.13 ~ 1.38 $mg\cdot L^{-1}$之间[25],在美洲的土壤和水中也检测到草甘膦的存在[26−27],其中加拿大地表水的草甘膦浓度达到 0.16 $mg\cdot L^{-1}$,阿根廷地表水的草甘膦浓度达到了 0.70 $mg\cdot L^{-1}$。此外,据报道,在农业盆地附近的不同河流和湖泊中草甘膦的浓度较高,如在阿根廷潘帕地区的浅水湖泊的地表水中检测到草甘膦浓度高达 4.52×10^{-3} $mg\cdot L^{-1}$[28],在布宜诺斯艾利斯北部的转基因大豆种植区附近的溪流中检测到的草甘膦含量在 0.10 ~ 0.70 $mg\cdot L^{-1}$之间[27]。类似现象不只出现在国外,我国国内也在不同的水环境中检测到草甘膦的残留。例如,广州珠江水源地中通过离子色谱法检测到草甘膦的浓度为 0.19 $mg\cdot L^{-1}$[29],重庆某鱼塘水中草甘膦的残留量高达 1.20 $mg\cdot L^{-1}$[30],甚至在浙江嘉兴、杭州、舟山和金华等地的饮用水中也检测到草甘膦的存在,浓度在 6.50×10^{-5} ~ 5.93×10^{-3} $mg\cdot L^{-1}$之间[31]。而与草甘膦生产或应用相关的工业所排放的废水中,草甘膦的残留浓度最高可达 0.75 ~ 0.90 $mg\cdot L^{-1}$[15, 32]。此外,草甘膦的主要代谢物氨甲基磷酸(AMPA)也经常在地表水[33]、地下水[34]和沉积物[35]中检测到。

2　草甘膦的环境行为(Environmental behaviors of glyphosate)

草甘膦会随着降雨形成的径流进入水源地或者通过渗透等途径进入到水环境中,然后在水环境中会通过吸附迁移、生物富集和降解等过程进行迁移转化,了解草甘膦的环境行为对于开展草甘膦的污染防治和防控具有非常重要的意义。

2.1　草甘膦的吸附-迁移行为

草甘膦和 AMPA(降解产物)可能通过风蚀作用转移到大气(空气或雨水)中,由于草甘膦为非挥发性化合物,所以这 2 种物质只能实现喷雾漂移或随风蚀沉积物迁移[36],喷雾漂移例如在除草剂的喷洒过程中会发生[2]。沉积物中草甘膦的浓度直接受附近施用源的影响,且与降雨事件有关联,通过表面雨水冲刷及风蚀作用使得草甘膦从施用源向地表水迁移[27]。此外,草甘膦向地表水迁移是高度可变的,草甘膦在植物体内不会发生降解,会通过植物的根系输送入土壤,因此取决于土壤颗粒的吸附水平,且这种吸附结合又基于土壤化学和物理特性的变化而变化[37],草甘膦或其降解产物可能作为溶质直接迁移或与土壤胶体共迁移(胶体促进或颗粒结合迁移),并通过土壤中的地下径流和地表径流移动,地下沥出物最终通过排水系统进入地表水,而地表径流输

送的物质会输入到开放水域，如溪流和湖泊[38-39]。草甘膦在底泥上的吸附作用较弱，在水生态系统中主要通过生物转化和分解作用实现迁移[40]。

2.2 草甘膦在水环境中的生物富集

生物富集是农药重要的环境行为之一，水生生物对草甘膦具有一定的生物富集能力。草甘膦在 20 ℃时的辛醇/水分配系数($\log K_{ow}$)为-3.2[41]，在水生生物中被认为其生物富集因子较低。朱国念等[42]通过模拟水域生态系统，发现^{14}C-草甘膦进入水系 20 d 时，其在金鱼藻(*Ceratopyllum demersum* L.)和麦穗鱼(*Psudorasobora parva*)中的活度分别为 241.91 $Bq\cdot kg^{-1}$ 和 396.16 $Bq\cdot kg^{-1}$，表明^{14}C-草甘膦在金鱼藻和麦穗鱼中有较强的富集作用。Wang 等[43]研究发现尽管草甘膦在阳光照射下 3 d 内消失，但是水葫芦中累积的草甘膦浓度在第 14 天时仍保持不变，而草甘膦在罗非鱼(*Oreochromis mossambicus*)和鲤鱼(*Cyprinus carpio*)体内累积的浓度在 2～7 d 时没有显著变化，表明草甘膦在水葫芦中有较强的富集作用，在罗非鱼和鲤鱼中富集作用较弱。

2.3 草甘膦的降解

由于草甘膦的大量使用造成水环境中的一定剂量的草甘膦及其代谢物残留，会给水环境中的生物甚至人类的健康带来潜在威胁，因此如何解决草甘膦的残留是问题的关键。草甘膦的降解可分为生物降解(其中最常见的是微生物降解)、氧化降解和光解等。

2.3.1 生物降解

生物降解被认为是从水环境中去除有机污染物最有效且生态的方法之一，其中最常见的是微生物降解[44]。水环境中的草甘膦通过微生物代谢分解成更小的分子，从而获得较高的去除率。草甘膦的微生物降解途径主要有 2 种：一是草甘膦被微生物降解为氨甲基磷酸(AMPA)和乙醛酸，这 2 种代谢物又进一步被降解为无机磷酸盐、CO_2 和铵离子；二是肌氨酸途径即草甘膦先被降解为无机磷酸盐和肌氨酸，肌氨酸然后进一步降解为甘氨酸[45-46]，甘氨酸经丝氨酸羟甲基转移酶作用进一步代谢为甲醛和甲醇[47]。有研究表明，这 2 种途径同时存在于一些细菌中，如：蜡样芽胞杆菌(*Bacillus cereus*)、假单胞菌属(*Pseudomonas*)等[46, 48]。已有研究显示对草甘膦降解效率较高的微生物包括假单胞菌属(*Pseudomonas*)[49-52]、黄杆菌属(*Flavobacterium*)[53]、链霉菌属(*Streptomyces* sp.)[54]、根瘤菌科(*Rhizobiaceae*)[55]和大肠杆菌(*Escherichia coli*)[56]等。刘攀[57]筛选出对草甘膦极端抗性的菌株淡紫拟青霉菌(*Paecilomyces lilacinus*) JLC71364，其抗性可达 1.01×10^5 $mg\cdot L^{-1}$。Obojska 等[58]观察到一种嗜热性钙氧硅藻土杆菌 T20 (*Gcillus caldoxylosilyticus* T20)在初始草甘膦浓度为 169 $mg\cdot L^{-1}$时，该细菌在 60 ℃时可实现超过 65%的草甘膦去除率并表明微生物培养条件(包括温度、初始 pH 值和草甘膦浓度等)的差异影响其降解性能。有研究也显示，由于水中的微生物比土壤中的少，水中草甘膦的降解速度比土壤的慢得多[59]。

2.3.2 光催化降解

光催化降解草甘膦的特点是成本低、程序易操作、应用广且二次污染小[60]。光降解可分直接和间接光解 2 种，直接降解是在光子作用下与有机物直接发生化学反应达到降解，间接降解其原理是在光的作用下，光催化剂吸收光子后发生能级跃迁即从基态跃迁成激发态，产生·OH 与有机物反应，最终将草甘膦降解为 H_2O、CO_2 等无毒小分子[60]。研究表明，ZnO、TiO_2 等金属氧化物纳米半导体材料在光催化下可降解有机污染物[61-62]。赵硕伟[63]研究发现经过 900 ℃煅烧的浓度为 0.5×10^3 $mg\cdot L^{-1}$的 ZnO 纳米粒子，光催化降解草甘膦 90 min 后草甘膦的去除率达 91.8%。杜沁媛[64]的研究中以 TiO_2 和 g-C_3N_4(半导体)为原料，用物理超声法合成 TiO_2/g-C_3N_4 二元复合光催化剂，结果表明添加 0.1 g 的质量比为 2∶8 的 TiO_2/g-C_3N_4 于 100 mL 浓度为 5 $mg\cdot L^{-1}$的草甘膦溶液中且模拟太阳光照射此体系 120 min 后，草甘膦的降解效率最佳，降解率可达到 91%；而当草甘膦溶液浓度是 3 $mg\cdot L^{-1}$时，模拟太阳光仅光照 60 min，降解率就高达到 98%；且在弱碱及中性条件下，降解率相对较高，pH=9 时，降解率为 98%；而在可见光照射下，TiO_2/g-C_3N_4 对草甘膦的降解效率比模拟太阳光的降解效率低 11%，表明体系中草甘膦溶液初始浓度、pH 及光源影响草甘膦的降解效率。

2.3.3 氧化降解

氧化处理有机污染物的物理化学反应中很少产生污染物，设备较简单且反应条件温和易控。处理水中草甘膦的高级氧化技术包括 O_3[65]、电极(DSA)氧化[66]、H_2O_2/UV[67]等化学方法。焦兆飞[68]研究发现单独使用 MnO_2 去除草甘膦时，MnO_2 的投入量越大、初始草甘膦浓度越低去除率越高，且利用电催化 MnO_2 氧化降解草甘膦比单独使用 MnO_2 的效果

更佳,更持久,对环境更友好。申元丽等[65]研究臭氧氧化降解草甘膦时发现其去除率与臭氧的投入量、草甘膦的初始浓度和初始的 pH 有关。杨帆等[69]采用次氯酸钠氧化与铁盐沉淀组合的工艺处理草甘膦,研究表明当次氯酸钠溶液投入量为 1.5 $mL \cdot L^{-1}$、pH=7、反应 1 h 时草甘膦的降解率达到 96.77%,且次氯酸钠溶液氧化后加入 $n(Fe^{3+})$∶n(P)为 1.2∶1 的铁盐沉淀(pH=5)时,可去除溶液中转化的无机磷及剩余的草甘膦,总磷去除率>99%。周长印[70]采用 Fenton 氧化法降解低浓度草甘膦,以纳米零价铁负载的 D201 (FeD201)为催化剂,研究表明当温度为 55 ℃、pH=5、H_2O_2 浓度为 170 $mg \cdot L^{-1}$、反应 1.5 h 时,初始浓度为 50 $mg \cdot L^{-1}$ 的草甘膦的降解率可达到 98% 以上。

3　草甘膦对水生生物的毒性(Toxicity of glyphosate on aquatic animals)

水生生物对草甘膦的敏感性较强,草甘膦的残留会对农业区池塘和湖泊等水环境中的水生生物存在潜在毒性[71-72],包括急性毒性[73]、神经毒性[74]、氧化毒性[75]、遗传毒性[76]和免疫毒性[77]等,草甘膦的残留会对鱼、虾、贝等一些非靶标生物造成危害,会威胁到水产养殖的可持续发展[19],草甘膦对水生生物的负面影响因此受到了广泛的关注[78]。

3.1　草甘膦对水生动物的毒性

3.1.1　急性毒性

研究草甘膦对水生生物的急性毒性是理解接触极限的关键点,目前已有较多关于草甘膦对水生动物的急性毒性研究。草甘膦对非洲革胡子鲶(*Clarias gariepinus*)的急性毒性试验中,24、48、72 和 96 h 的半致死浓度(LC_{50})值分别为 34.72、31.90、27.40 和 24.60 $mg \cdot L^{-1}$,草甘膦暴露下的幼鱼行为异常,例如,失去平衡、跳出水面、鳃盖运动减少等,随后死亡,且死亡率随草甘膦暴露时间和浓度的增加而增加[73]。史建华等[79]在草甘膦对中华绒螯蟹(*Eriocheir sinensis*)的急性毒性试验中,发现草甘膦在 12、24、36 和 48 h 时对中华绒螯蟹的 LC_{50} 分别为 18.91、16.67、13.99 和 12.09 $mg \cdot L^{-1}$,草甘膦对中华绒螯蟹的毒性为低毒[80]。然而,草甘膦对草鱼(*Ctenopharyngodon idella*)、鲢鱼(*Hypophthalmichthys molitrix*)和鲫鱼(*Carassius auratus auratus*)的 96 h-LC_{50} 分别为 0.2518、0.2588 和 0.2599 $mg \cdot L^{-1}$,毒性属于高毒[81]。甚至有研究表明草甘膦对泥鳅(*Misgurnus anguillicaudatus*)等无鳞鱼类的毒性更大,对泥鳅体内的淋巴细胞分化有一定的影响,过量使用会导致泥鳅绝迹[82]。

3.1.2　神经毒性

中枢神经系统是神经系统的重要组成部分,有传递、储存和加工信息的功能,且神经系统和神经行为关系十分密切,可支配和控制动物的全部行为[83]。胆碱能受体在整个中枢神经系统中差异表达、基因表达的调控和神经递质的释放中均起重要的作用[84]。有机磷农药草甘膦可影响水生生物神经系统的传导,从而产生神经毒性作用[85]。有研究表明,氧化应激、神经递质分布和行为的变化是草甘膦对中枢神经系统的一些诱导效应[86-87]。Faria 等[88]研究发现,在浓度为 3×10^{-4} $mg \cdot L^{-1}$ 和 3×10^{-3} $mg \cdot L^{-1}$ 的草甘膦中暴露 2 周后,斑马鱼(*Danio rerio*)成鱼的前脑多巴胺和血清素水平显著增加,以及多巴胺能系统相关的基因如 *th1*、*th2*、*comtb* 和 *scl6a3* 的表达量下调,且大脑表现出氧化应激,即过氧化氢酶(CAT)和超氧化物歧化酶(SOD)活性增加,谷胱甘肽(GSH)储存量减少,且草甘膦暴露下的斑马鱼成鱼表现出明显的行为异常,表明低浓度的草甘膦暴露会诱发神经毒性。Paganelli 等[89]的研究表明,草甘膦除草剂的使用会引起爪蟾(*Xenopus tropicalis*)神经嵴发育和初级神经元分化异常、后脑菱形图案丢失、维甲酸途径失调引起包括视泡减少和小头畸形等,而最终导致爪蟾身体、大脑和眼睛发育异常。Roy 等[90]研究草甘膦和农达暴露对斑马鱼仔鱼的影响,发现斑马鱼前脑和中脑 *pax2*、*pax6*、*otx2* 和 *ephA4* 基因表达量减少,即表明草甘膦和农达制剂对前脑和中脑具有神经毒性。乙酰胆碱酯酶(AchE)活性被用作神经毒性的经典生物标志物[91-92],有研究也发现,暴露于草甘膦的鲤鱼(*Cyprinus carpio*),其体内 AchE 的活性受到了抑制[93-94],表明草甘膦对鲤鱼具有明显的神经毒性作用。

3.1.3　氧化毒性

环境污染物草甘膦可影响生物机体的抗氧化防御系统,并通过产生活性氧对水生生物造成氧化损伤[95-96]。受到污染物的低浓度暴露时,为了使机体免受氧化损伤,抗氧化酶会被激活,消除过量的自由基;但当污染物浓度超过机体耐受域值,多余未被清除的自由基会使细胞衰老加速,导致酶活降低[97]。有研究表明,氧化应激可能是草甘膦对动物毒性的机制之一[98]。例如,草甘膦亚致死剂量的暴露会诱

导翠鳢(*Channa punctatus*)的氧化应激,导致脂质过氧化产物(LPO)升高,抑制了抗氧化酶并且诱导遗传毒性[99]。在急性接触商业草甘膦制剂的蝌蚪中,发现谷胱甘肽转移酶(GST)的活性降低[100],同样在相似浓度刺激下会导致条纹鲮脂鲤(*Prochilodus lineatus*)和克林氏鲶鱼(*Rham diaquelen*)的 GST 的活性升高或降低[101-102]。Sobjak 等[103]将克林氏鲶鱼暴露于草甘膦中,发现 12 h 时胆碱酯酶(ChE)和谷胱甘肽还原酶(GR)的活性均受到诱导,72 h 时,CAT、GR、LPO 产物及 ChE 等均受到抑制,表明草甘膦的急性暴露能引起克林氏鲶鱼抗氧化系统的异常变化和发育毒性。此外,Hong 等[104]将日本沼虾(*Macrobrachium nipponensis*)暴露于 0.35、0.70、1.40、2.80 和 5.60 $mg \cdot L^{-1}$的草甘膦亚致死浓度下 9 h 时,除 0.35 $mg \cdot L^{-1}$浓度组外,其他处理组的 SOD、CAT 和总抗氧化能力均呈剂量和时间依赖性下降,而血清中丙二醛(MDA)、过氧化氢和蛋白质羰基含量在 2.80 $mg \cdot L^{-1}$和 5.60 $mg \cdot L^{-1}$浓度下显著升高,表明草甘膦对日本沼虾具有显著的氧化毒性作用。

3.1.4 遗传毒性

水环境中的污染物作用于有机体时,可能会使其遗传物质在分子水平、染色体水平和碱基水平上受到各种损伤因而造成遗传毒性。遗传毒性分为 DNA 损伤、基因突变、染色体结构和数目的改变[105-106]。草甘膦的遗传毒性主要通过彗星试验、微核试验和红细胞异常试验进行评估,这些试验分别确定了 DNA 双链断裂的数量、诱发的染色体损伤和红细胞核异常[107]。袁建军等[108]研究发现在 53.5 $mg \cdot L^{-1}$的草甘膦染毒 8 d 后,大弹涂鱼(*Boleophthalmus pectinirostris*)红细胞微核率及核异常率分别为 17.00‰和 21.33‰,均显著($P<0.01$)高于相应对照值(13.67‰和 13.33‰),且随草甘膦染毒浓度的增大,其红细胞微核率及核异常率均显著升高,表明草甘膦对大弹涂鱼具有遗传毒性。陈建华等[109]研究发现草甘膦能诱发斑马鱼外周血红细胞微核及核异常,提示草甘膦对斑马鱼具有遗传毒性。有研究表明,活性氧依赖的 DNA 损伤是草甘膦遗传毒性的主要机制[110]之一。在 10 $mg \cdot L^{-1}$的草甘膦中暴露 6 h,条纹鲮脂鲤的 DNA 完整性就受到了较大的影响[77],但随时间的推移这些影响会减弱,表明草甘膦对 DNA 的损伤大多数发生在接触后不久,且这种模式可以用 DNA 修复系统的参与和解毒途径的激活来缓解[111]。也有研究发现,在浓度为 0.005 $mg \cdot L^{-1}$的草甘膦溶液中暴露 1 h 后,牡蛎(*Ostrea gigas* Thunberg)的精子中并未发现双键断裂,表明遗传毒性的程度与物种、草甘膦的暴露浓度以及暴露时间有关[112]。

3.1.5 免疫毒性

在被污染物干扰的过程中,免疫系统的响应可能是更敏感的生理反应之一[113]。免疫系统通过清除外来物质(病毒、细菌或寄生虫)来帮助宿主保持体内平衡,杀死异常细胞,排斥“非自身”成分[113]。污染物或外来物质与免疫系统成分相互作用,干扰保护功能,被称为免疫毒性[114]。外源性物质可引起免疫抑制或刺激、自身免疫和抗病能力下降[115]。有研究表明,银鲶(*Rhamdia quelen*)在暴露于亚致死浓度的草甘膦后,细胞数量和吞噬指数显著下降,因此除草剂在水中的存在可能会改变机体对细菌以及可能对其他水生微生物的天然免疫反应[116]。有学者研究草甘膦除草剂对 8 月龄幼年欧洲海鲈(*Dicentrarchus labrax*)鳃、肠和脾脏中 *il-1β*、*il-10* 和 *ho-1* 基因表达的影响,发现在 647 $mg \cdot L^{-1}$的农达暴露 96 h 时,欧洲海鲈肠道的 *il-1β* 和 *il-10* 细胞因子变化不显著,但在鳃中这 2 种因子的水平显著降低,*ho-1* 基因的表达水平则在 3 种组织中都显著增加,提示农达对欧洲海鲈的免疫系统产生负面影响[117]。有研究也显示,太平洋牡蛎在环境相关浓度的草甘膦暴露 7 d 后,其血细胞的吞噬作用会降低,血细胞的功能下调,特别是抑制有吞噬作用基因的表达,还会增加对细菌攻击的敏感性[118]。对鲤鱼的研究表明,在 104.15 $mg \cdot L^{-1}$的草甘膦中暴露 168 h 时,鲤鱼肾脏中免疫球蛋白 M(*IgM*)、补体 *C3* 和溶菌酶(*LYZ*)的转录水平发生了改变,表明草甘膦可通过抑制 *IgM*、*C3* 和 *LYZ* 的表达以及通过损伤鱼肾而对鲤鱼产生免疫毒性[119]。

3.2 草甘膦对水生植物的毒性

草甘膦是一种灭生性除草剂,对水生植物具有重要的致毒作用。草甘膦会显著下调沉水植物苦草(*Vallisneria natans*)的叶绿素、类胡萝卜素和可溶性蛋白含量及 CAT 活性,且黑藻(*Hydrilla verticillata*)对于草甘膦的敏感性高于苦草,可能会破坏水生植物群落结构的稳定[120]。有研究表明,草甘膦对浮游植物群落结构组成有直接的毒性[121]。研究表明 0.08 $mg \cdot L^{-1}$的草甘膦会显著降低浮萍的生长率和叶绿素 *a* 荧光参数[122],1 $mg \cdot L^{-1}$的草甘膦会影响浮萍的叶片的生长速率和数量以及形态结构[123]。另

有研究表明,在温室条件下,一定剂量的草甘膦抑制凤眼莲(*Eichhornia crassipes*)、槐叶苹(*Salvinia natans*)等水生漂浮植物的生长[124],表明草甘膦对水生漂浮植物具有毒性。有学者发现,草甘膦会抑制铜绿微囊藻(*Microcystis aeruginosa*)的生长,影响蛋白质的合成,并使抗氧化系统受到损伤[125-126]。王洪斌等[127]探索了草甘膦染毒对塔胞藻(*Pyramidomonas delicatula*)和塔玛亚历山大藻(*Alexandrium tamarense*)这 2 种藻类的叶绿素含量以及 MDA 含量、SOD、CAT 活性的影响,发现草甘膦浓度>6 $mg \cdot L^{-1}$ 时会抑制 2 种藻类细胞中叶绿素的含量,且随草甘膦浓度升高叶绿素含量越低;SOD 的活性表现出了先诱导后抑制的现象,CAT 活性则表现出微弱的抑制效应,表明草甘膦对这 2 种藻类有氧化毒性效应。

3.3　草甘膦对水生微生物的毒性

水生微生物在生态系统中扮演重要角色,所以当水环境接触到草甘膦或许会影响某些水生微生物的群落结构和生存[128],然而,目前草甘膦对水生微生物的研究仍较为匮乏。虽有研究表明 0.01 $mg \cdot L^{-1}$ 的草甘膦对河流微生物群落结构有影响[129],但与许多其他种类的农药一样,草甘膦对水生细菌和原生动物的毒性数据仍较为缺乏,大多数是关于藻类的[130]。最近的一项研究表明,草甘膦会延迟周生植物的定居,减少硅藻(*Bacillariophyta*)的丰度,并促进浅水湖泊中蓝藻的生长[131]。有研究表明,草甘膦会与水生病原菌或病毒协同作用,降低鱼类存活率[132]。海龟(*Chelonia mydas*)与 4 种安乐死的海龟肠道细菌(泛菌(*Pantoea*)、变形杆菌(*Proteus*)、葡萄球菌(*Staphylococcus*)及志贺氏菌(*Shigella*))混合培养物暴露于不同浓度的草甘膦下 24 h,当草甘膦的浓度>0.22 $mg \cdot L^{-1}$时,细菌密度显著降低,当草甘膦的浓度>1.76 $mg \cdot L^{-1}$时,4 种海龟肠道细菌生长受到显著抑制且存活率下降,表明草甘膦对水生生物的肠道细菌也有毒性作用[133]。

4　总结与展望(Conclusion and prospect)

草甘膦在除草过程中受到广泛使用,并会通过许多途径进入水环境中,对水环境及水生生物健康造成威胁。目前,草甘膦在水环境中的环境行为和对水生生物的毒性研究表明:草甘膦会通过各种途径吸附-迁移并富集在水生生物体内,其在水环境中降解速度非常缓慢,在多地水体中均检测到草甘膦的残留;草甘膦的残留会对非靶标水生生物造成危害,包括急性毒性、神经毒性、氧化毒性、遗传毒性和免疫毒性等。我国是草甘膦的使用大国,目前有关草甘膦的来源、污染现状及水环境行为已得到较为深入的研究,但关于草甘膦对水生生物毒性作用方面的研究仍存在许多亟待解决的问题:(1)国内外对草甘膦的中间产物及其代谢产物对水生生物的毒性研究欠缺,因此开展这些物质对非靶标水生生物的毒性研究有利于全面地揭示草甘膦的致毒机理,是今后研究的重点之一;(2)目前用于草甘膦毒性效应研究的水生生物种类较为局限,然而不同种类的水生生物对草甘膦的敏感性存在较大的差异,因此今后需进一步加强草甘膦对多种水生生物或不同营养级水生生物毒性效应的研究;(3)在实际应用过程中,草甘膦与其他除草剂常常联合使用以达到更好的防治效果,因此,在今后的研究中应重视草甘膦联合用药对水生生物的毒性作用机制,才能为草甘膦的水生生态毒性和环境风险评估提供科学依据,为草甘膦的合理使用提供理论指导。

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