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硫丹的环境行为及水生态毒理效应研究进展

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摘要: 有机氯农药硫丹作为一种典型的持久性有机污染物(POPs)曾广泛应用于农业生产,我国曾大量使用。硫丹作为一种重要的污染物通过地表径流、淋、溶、干/湿沉降等方式进入水体,在直接影响大型水生植物和浮游藻类的同时,给鱼类等水生动物也带来了一定的毒性效应。由于其半衰期较长、迁移能力强、富集性高,在水体环境中已普遍检测出硫丹的存在,因此,对硫丹的水生生态安全性评价显得十分重要。硫丹对水生生物具有高毒性,它可影响生物正常受体配体作用、损伤生物膜、影响活性氧代谢并具有潜在的内分泌干扰作用。本文介绍了硫丹的环境行为效应,并综述了硫丹对水生生物的毒性及几种致毒机制,展望了该领域今后的研究重点和方向。

关键词: 硫丹;POPs;水生生物;环境行为;毒理效应

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Research Progress in the Environmental Behavior and Water Ecotoxicological Effects of Endosulfan

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Abstract: As a typical persistent organic pollutants, endosulfan, the organochlorine pesticide, has been widely used in agricultural production in China. Endosulfan could go into the water environment through the surface runoff, leaching and wet/dry deposition, which will have a direct impact on aquatic macrophytes and planktonic algae, and produce a certain amount of toxic effects on fish and other aquatic animals as well. Because of its longer half-life period, better migration abilities and higher enrichment, endosulfan could be detectable widely in the water body, herein the safety evaluation of endosulfan in the aquatic ecosystem is very important. Endosulfan is so highly-toxic to aquatic organisms that it could have influences on normally biological receptor-ligand function, membrane damage, active oxygen metabolism and have a potential role of en-

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docrine disruption. The environmental behavior effects and several toxic mechanisms of endosulfan on aquatic organisms will be reviewed, and the future prospects in this filed will be also discussed.

Keywords: endosulfan; POPs; aquatic organisms; environmental behaviors; toxicology effects

硫丹(endosulfan)分子式: $C_9H_6Cl_6O_3S$, 又称赛丹或安赛丹, 纯品为白色晶体, 易溶于氯仿、丙酮等有机溶剂。其在碱性介质中不稳定, 可缓慢水解为硫丹二醇和二氧化硫, 常见的 α -硫丹和 β -硫丹 2 种异构体混合物比例约为 7:3^[1]。作为一种危害性极高的有机氯农药, 硫丹曾广泛用于棉花、烟草、茶叶和咖啡等农业生产中。据统计, 全世界范围使用硫丹总量为 30.8 万 t^[2-3]。由于具有较强的迁移作用, 硫丹在生产、使用和废弃过程中可通过污水、废水、地表径流或大气沉降等最终进入水环境中, 且其在水体中的浓度水平危及水生生物和人类的健康, 因此硫丹在水体中的分布及其对水生生物的毒理效应一直是人们关注的焦点^[4]。然而从目前资料来看, 关于硫丹在环境中的分布情况研究较多, 而硫丹对水生生物的生理生化、内分泌毒性、遗传毒性及代谢机制等方面研究较少。本文综述了近年来硫丹的环境行为及对水生生物的毒性作用研究, 并分析今后的研究思路, 对以后的研究热点做了展望。

1 概 述

1.1 硫丹的环境行为及分布

环境中硫丹有 2 个来源: 一是硫丹在农业生产中大量使用, 使一部分硫丹挥发进入大气, 另一部分是黏附在农作物上的硫丹在雨水冲刷、淋溶及地表径流的作用下, 被转运至土壤和水体中; 二是硫丹生产工厂废弃污染物排放使硫丹进入水体和土壤环境中。

硫丹 2 种异构体均可被氧化、水解为硫丹硫酸盐(endosulfan sulphate)和硫丹二醇(endosulfan diol)^[5]。

硫丹具有较强的环境迁移能力, 据报道, 硫丹作为一种有机氯农药广泛存在于大气环境中, 并可随大气环流迁移到全球各个地区, 高山地区、极地地区环境介质中均发现硫丹及硫丹硫酸盐存在。Pozo 等^[6]检测到智利北部大气硫丹浓度为 4 ~ 101 $pg \cdot m^{-3}$, 并发现硫丹主要生产使用地的北部地区大气硫丹含量高于南部地区。加拿大西部高山地区大气中也检测出硫丹存在, 且 α -硫丹浓度高于 β -硫丹浓度^[7]。我国大气中同样发现硫丹, 通过对我国的 37 个城市及 3 个背景点的空气中有有机氯进行分析, α -硫丹和 β -硫丹的浓度范围分别为 0 ~ 1 190 $pg \cdot d^{-1}$ 和 0 ~ 422 $pg \cdot d^{-1}$ ^[8], 同时发现, 含量较高采样点出现在棉花种植区, 表明农业使用是我国空气中硫丹的重要来源。

水环境中同样有硫丹的存在, 我国太湖中也检测出硫丹, 表 1 列出了世界上部分典型水体中硫丹的含量。

美国高海拔(3 024 ~ 3 030 m)湖泊沉积物中也检测出硫丹硫酸盐存在^[13]。研究发现加拿大北极圈群岛 Devon 岛 DV09 地平线以上湖底沉积物中有 α -硫丹存在, 最高浓度达 0.04 $ng \cdot g^{-1}$ (干重), 且流量为 6.2 $ng \cdot (m^2y)^{-1}$, 自 1990 年起, 这些湖泊沉积物硫丹含量在逐渐增加^[14]。

表 1 硫丹在部分水环境中的浓度
Table 1 The concentration of endosulfan in the water environment

硫丹浓度 Concentration of endosulfan	α -硫丹 α -endosulfan	β -硫丹 β -endosulfan	硫丹硫酸盐 endosulfan sulfate	总硫丹 Total of endosulfan
加拿大北极圈群岛 ^[9] Canada Arctic Islands ^[9]	0.42 $ng \cdot L^{-1}$	-	-	-
北冰洋海水 ^[10] The Arctic Ocean ^[10]	2.3 $pg \cdot L^{-1}$	1.5 $pg \cdot L^{-1}$	6.9 $pg \cdot L^{-1}$	10.7 $pg \cdot L^{-1}$
加拿大 Hazen 湖 ^[11] Hazen Lake of Canada ^[11]	1.4 $pg \cdot L^{-1}$	0.7 $pg \cdot L^{-1}$	18.9 $pg \cdot L^{-1}$	20.9 $pg \cdot L^{-1}$
加拿大 Char 湖 ^[11] Char Lake of Canada ^[11]	2.8 $pg \cdot L^{-1}$	1.5 $pg \cdot L^{-1}$	31.6 $pg \cdot L^{-1}$	35.9 $pg \cdot L^{-1}$
中国太湖 ^[12] Taihu Lake of China ^[12]	0.32 $pg \cdot L^{-1}$	-	-	-

1.2 硫丹在水生生物体内的蓄积

研究报道,水生生物体内也已普遍检测出硫丹。其中,我国华南沿海牡蛎(*Crassostrea rivularis*)体中硫丹含量为广东:2.13 ng·g⁻¹(湿重),海南:1.23 ng·g⁻¹(湿重),广西:0.76 ng·g⁻¹(湿重)^[15]。Kelly 等^[16]发现北极红点鲑(*Salvelinus alpinus*)、环斑海豹(*Phoca hispida*)和白鲸(*Delphinapterus leucas*)体内 α-硫丹和 β-硫丹含量分别为(0.12 ± 0.09) ng·g⁻¹(湿重)、(0.46 ± 0.55) ng·g⁻¹(湿重);(2.0 ± 3.2) ng·g⁻¹(湿重)、(1.7 ± 2.1) ng·g⁻¹(湿重)和(4.0 ± 5.9) ng·g⁻¹(湿重)、(6.5 ± 2.8) ng·g⁻¹(湿重)。而 Stern 等^[24]发现加拿大北极群岛雄性白鲸体内硫丹硫酸盐含量从 3.7 ng·g⁻¹(脂重)到 94 ng·g⁻¹(脂重)不等。加拿大北极群岛 Lancaster 海峡和 Jones 海峡雄性白鲸体内(28 ~ 94 ng·g⁻¹)发现更高浓度的硫丹硫酸盐,而 Baffin 岛 Cumberland 海峡和 Frobisher 湾的白鲸体内硫丹硫酸盐的含量为 8.1 ~ 23 ng·g⁻¹。据报道,印度超过 60% 的市售海水鱼可检测出硫丹,其浓度为 5 ~ 22 ng·g⁻¹(湿重)^[17]。大量研究显示,硫丹及其降解产物主要在动物的肝脏、皮肤、脂肪及肌肉中分布^[18]。可见,除了毒物代谢器官,脂肪及皮肤也是硫丹主要分布区域,这可能是因为硫丹的辛醇—水分配系数(logK_{ow})显示其进入富含脂肪组织中的可能性较大,并可随着胚胎中脂肪转运进入卵细胞或者传递给下一代。

硫丹在水生生物体内的浓度水平能直接反映水体中硫丹的污染情况,进而可以评价其对生态系统的潜在危害。有研究表明,水体中 β-硫丹较 α-硫丹含量更高,这或许表明 α-硫丹更容易被水生生物转化、富集^[19]。α-硫丹、β-硫丹的 logK_{ow} 分别为 4.94 和 4.78,因此沉积物对 α-硫丹的吸附作用较 β-硫丹强,α-硫丹生物富集能力略强于 β-硫丹^[20]。一般认为当有机化合物 logK_{ow} > 5 时,该化

合物具有生物富集性。浮游动物比浮游植物更易富集硫丹,而鱼类对硫丹富集能力明显大于浮游生物^[21]。生物富集系数(BCF)经常用来评价污染物在水生生物体内的富集效果。研究表明,黄脂鲤鱼(*Hyphessobrycon bifasciatus*)对硫丹 BCF 高达 11 000^[22],淡水绿藻(*Pseudokirchneriella subcapitata*)和淡水大型蚤(*Daphnia magna*)对硫丹 BCF 分别为 2 682 和 3 678^[23],而野鲮(*Labeo rohita*)对硫丹 BCF 只有不到 50^[24],因此不同生物对硫丹富集能力存在较大差别。

2 硫丹的水生生物毒性效应

不同形态的硫丹在环境中的降解速率不同,生物毒性也不相同。β-硫丹较 α-硫丹降解慢,α-硫丹半衰期为 7 ~ 75 d,而 β-硫丹半衰期为 33 ~ 376 d,研究表明,硫丹硫酸盐是环境中硫丹的主要降解产物^[25]。水中 α-硫丹较 β-硫丹更易降解为硫丹硫酸盐^[26],在土壤环境中也有同样发现,并且硫丹降解速率受土壤水分、温度、含氧量、pH 等环境因素影响,温度较低、水分较小、含氧量低、pH 较低情况下硫丹的降解速率较慢^[27]。硫丹降解产物毒性较小,如:硫丹硫酸盐对金鱼(*Carassius auratus*)和雅罗鱼(*Leuciscus idus melanotus*)48 h 半数致死浓度(48 h LC₅₀)接近 100 μg·L⁻¹,而 α-硫丹 < 10 μg·L⁻¹^[28]。另外,硫丹与其他污染物的联合毒性效应更强。资料显示,394 μg·L⁻¹毒死蜱与 4.5 μg·L⁻¹、7.9 μg·L⁻¹、1 μg·L⁻¹ 硫丹共同作用下,太平洋树蛙幼体(*Pseudacris regilla*)致死率显著高于硫丹单一染毒^[29]。

2.1 硫丹的急性致毒效应

几乎所有水生生物对硫丹都非常敏感。水生无脊椎动物是水生动物中较低等的动物类群,表 2 列出了硫丹对一些水生无脊椎动物的毒性值。

表 2 硫丹对甲壳类动物毒性
Table 2 Toxicity of endosulfan on shellfish

LC ₅₀ /EC ₅₀	24 h LC ₅₀	48 h LC ₅₀	96 h LC ₅₀	24 h EC ₅₀
大型蚤(<i>Daphnia magna</i>) ^[30-23]	-	950 μg·L ⁻¹	-	336 μg·L ⁻¹
马氏沼虾(<i>Macrobrachium malcolmonii</i>) ^[31]	-	-	0.16 μg·L ⁻¹	-
斑节对虾(<i>Penaeus monodon</i>) ^[32]	-	-	0.61 μg·L ⁻¹	-
桃红对虾(<i>Penaeus duorarum</i>) ^[33]	-	-	0.004 μg·L ⁻¹	-
短刀小长臂虾(<i>Palaemonetes pugio</i>) ^[34]	-	-	0.62 μg·L ⁻¹	-
淡水钩虾(<i>Gammarus lacustris</i>) ^[35]	-	-	5.8 μg·L ⁻¹	-
石蝇(<i>Pteronarcys</i> sp.) ^[35]	-	-	3.3 μg·L ⁻¹	-
中华绒螯蟹(<i>Eriocheir sinensis</i>) ^[36]	1.66 mg·L ⁻¹	0.9 mg·L ⁻¹	-	-

研究表明,硫丹对藻类也有较高毒性,硫丹对近头状伪蹄型藻(*Pseudokirchneriella subcapitatum*)96 h EC₅₀为 428 μg·L⁻¹ [23]。此外,有研究显示,不同的环境条件也可能影响硫丹对甲壳动物的毒性。当暴露环境中有底泥存在时,硫丹对褐虾(*Penaeus aztecus*)96 h LC₅₀从无底泥存在时的 0.2 μg·L⁻¹ 提高到 6.9 μg·L⁻¹ [37];斑节对虾(*Penaeus monodon*)96 h LC₅₀从无底泥存在时的 1.6 μg·L⁻¹降低到 0.5 μg·L⁻¹;96 h 最低可观察效应浓度(LOEC)从无底泥存在时的 1.038 μg·L⁻¹降低到 0.141 μg·L⁻¹;96 h 最低无可观察效应浓度(NOEC)从无底泥存在时的 0.536 μg·L⁻¹降低到 < 0.141 μg·L⁻¹ [38]。0.1 μg·L⁻¹ 硫丹暴露 96 h,美洲龙虾幼体(*Homarus americanus*)代谢范围较对照组显著降低 25% [39]。

硫丹对鱼类同样具有较强毒性。研究显示,硫丹对大部分鱼类的 96 h LC₅₀为 0.09~4.4 μg·L⁻¹ [40],且淡水鱼类相对海水鱼类具有更高的耐受性,见表 3。

根据毒性分级,LC₅₀ < 1 000 μg·L⁻¹ 为剧毒物质。绝大部分鱼类对硫丹极为敏感,96 h LC₅₀ 均在 10 μg·L⁻¹ 以下,可见硫丹对鱼类毒性极强。硫丹对不同鱼类 LC₅₀ 有所差异,可能原因有 2 种:一是受试动物对硫丹的耐受程度不同,二是暴露试验的环境条件不同。另外,研究发现,高等鱼类较低等鱼类对硫丹的耐受能力更强一些,这可能是因为高等鱼类的代谢器官更为发达、解毒系统更为完善,使毒物对机体的毒性作用更小。

2.2 干扰正常受体—配体的相互作用

受体是许多组织细胞的生物大分子,与化学物质即配体相结合后形成受体—配体复合物,能产生一定

的生物学效应。许多毒物尤其是某些神经毒物的毒性作用与其干扰正常受体—配体相互作用的能力有关。

目前有研究表明,硫丹可与 γ-氨基丁酸(GABA)拮抗,从而抑制 GABA 受体聚集 [45]。GABA 是中枢神经系统抑制性神经递质,硫丹作为 GABA 非竞争性的拮抗物,可抑制 GABA 受体聚集,聚集程度的降低将导致神经元细胞去极化,使动物焦躁不安 [46]。

胆碱能神经是以乙酰胆碱(ACh)为神经传递物质,在 ACh 完成传递任务后,若继续存在,则将不断刺激突触后膜,引起神经功能的紊乱,因此必须及时将之分解消除,这有赖于乙酰胆碱酯酶(AChE)对 ACh 的催化作用,AChE 可将 ACh 分解为乙酸和胆碱,避免 ACh 积累对神经的过多刺激。有机磷农药已被证实可抑制动物胆碱酯酶(ChE)活性,使其失去分解 ACh 能力,导致 ACh 积聚,阻断神经传导,引起神经功能紊乱 [51]。研究显示,3.3~5 μg·L⁻¹ 硫丹暴露 96 h,可显著抑制橙色莫桑比克罗非鱼(*Oreochromis mossambicus*)脑 AChE 活性 [52]。同样发现,0.072~1.4 μg·L⁻¹ 硫丹暴露,可显著抑制四眼青鳉(*Jenynsia multidentata*)肌肉 AChE 活性,并发现随着硫丹暴露质量浓度升高或时间延长,其活动能力明显下降,游泳能力受到显著影响 [53]。2.4 μg·L⁻¹ 硫丹暴露 96 h,斑马鱼脑 AChE 活性显著降低,较对照组下降近 40%,其活动能力同样显著降低 [54]。

2.3 生物膜损伤作用

生物膜具有十分重要的生物功能,它可选择地进行物质交换,以维持细胞内部有一个相对稳定的理化特性,并维持细胞内自身稳定。Na⁺、K⁺-ATP 酶和 Ca²⁺、Mg²⁺-ATP 酶又称依赖 ATP 膜结合蛋

表 3 硫丹对部分鱼类的 LC₅₀
Table 3 LC₅₀ of endosulfan on fish

LC ₅₀	24 h LC ₅₀	48 h LC ₅₀	72 h LC ₅₀	96 h LC ₅₀
翠鳢(<i>Channa punctatu</i>) [41]	19.7 μg·L ⁻¹	13.0 μg·L ⁻¹	10.2 μg·L ⁻¹	7.8 μg·L ⁻¹
虹鳟(<i>Oncorhynchus mykiss</i>) [42]	19.8 μg·L ⁻¹	4.24 μg·L ⁻¹	8.9 μg·L ⁻¹	2.49 μg·L ⁻¹
斑马鱼(<i>Danio rerio</i>) [43]	5.3 μg·L ⁻¹	1.77 μg·L ⁻¹	1.8 μg·L ⁻¹	1.62 μg·L ⁻¹
黄鳝(<i>Monopterus albus</i>) [44]	-	-	-	0.42 μg·L ⁻¹
黑头软口鲮(<i>Pimephales promelas</i>) [45]	-	-	-	1.4 μg·L ⁻¹
银鲈(<i>Lateolabrax japonicus</i>) [35]	-	-	-	2.4 μg·L ⁻¹
葛氏鲈塘鳢(<i>Perccottus glenii</i>) [46]	18.58 μg·L ⁻¹	12.46 μg·L ⁻¹	11.38 μg·L ⁻¹	7.59 μg·L ⁻¹
草鱼(<i>Ctenopharyngodon idellus</i>) [47]	3.82 μg·L ⁻¹	2.52 μg·L ⁻¹	1.86 μg·L ⁻¹	1.42 μg·L ⁻¹
食蚊鱼(<i>Gambusia affinis</i>) [48]	6.033 μg·L ⁻¹	3.647 μg·L ⁻¹	2.617 μg·L ⁻¹	2.273 μg·L ⁻¹
玛丽鱼(<i>Poecilia latipinna</i>) [48]	8.429 μg·L ⁻¹	5.035 μg·L ⁻¹	4.257 μg·L ⁻¹	3.506 μg·L ⁻¹
福尔摩莎鳉(<i>Heterandria formosa</i>) [48]	4.156 μg·L ⁻¹	2.566 μg·L ⁻¹	2.183 μg·L ⁻¹	2.058 μg·L ⁻¹

白酶,对建立跨膜的离子梯度、维持细胞膜电位与细胞生理活动、调节细胞渗透压、控制细胞容量和正常代谢以及为其他离子和营养物质的转运提供动力方面具有重要作用^[55]。

研究表明,硫丹可影响鱼类 ATP 酶活性,从而影响细胞正常生物功能。2.2 $\mu\text{g}\cdot\text{L}^{-1}$ 硫丹暴露 15 d,可激活宽额鳊(*Channa gachua*) Na^{+} 、 K^{+} -ATP 酶和 Mg^{2+} -ATP 酶活性;3.7 $\mu\text{g}\cdot\text{L}^{-1}$ 硫丹暴露 30 d 后,其肝脏、肾脏及肌肉 ATP 酶活性显著受到抑制^[56]。暴露于 0.010 ~ 0.264 $\mu\text{g}\cdot\text{L}^{-1}$ 硫丹下,罗氏沼虾仔虾(*Macrobrachium rosenbergii*) Na^{+} 、 K^{+} -ATPase 活性显著升高^[57]。翠鳢(*Channa punctatus*)鳃 Na^{+} 、 K^{+} -ATP 酶活性在 1.2 $\mu\text{g}\cdot\text{L}^{-1}$ 硫丹暴露 90 d 后明显降低^[58]。大西洋鲑(*Salmo salar*)硫丹(4 ~ 710 $\mu\text{g}\cdot\text{kg}^{-1}$)经口染毒 14 d,鳃 Na^{+} 、 K^{+} -ATP 酶活性明显降低,35 d 后恢复到正常水平;肠 Na^{+} 、 K^{+} -ATP 酶活性 14 d 和 35 d 均被显著抑制^[59]。Velasco 等^[60]报道,0.16 $\mu\text{g}\cdot\text{L}^{-1}$ 和 0.48 $\mu\text{g}\cdot\text{L}^{-1}$ 硫丹暴露 14 d,可引起斑马鱼 Na^{+} 、 K^{+} -ATP 酶活性升高,并在 28 d 后恢复到正常水平,同时发现其鳃丝组织增生。

2.4 活性氧生成与氧化损伤机理

活性氧(ROS)是指在生物体内与氧代谢有关的含氧自由基和易形成自由基的过氧化物总称,如 $\text{O}_2^{\cdot-}$ 、 $\cdot\text{OH}$ 、 H_2O_2 、 ROOH 等。生物体自身生理活动可产生 ROS,如分解氧以提供能量的电子传递链过程、吞噬细胞吞噬作用以及外源物质的分解过程,污染物也可诱导生物细胞内外源性 ROS 形成^[61]。

体内的 ROS 具有一定的功能,如免疫和信号转导过程,但由于它有未成对电子,自由基和自由原子非常活泼,因此过多的 ROS 就会有破坏作用,导致正常细胞和组织的损坏。正常情况下细胞内的抗氧化酶类 SOD、CAT、GSH-Px 等可以清除 ROS,而当 ROS 的产生与清除平衡被扰乱,细胞无法及时清除时,就会导致机体氧化损伤^[62]。ROS 过量生成可干扰多种信号转导通路,从而影响细胞凋亡,如 MAPKs 信号通路、ERK1/2 通路、Nrf2-Keap1 通路、JNK/SPAK 通路等。研究表明,硫丹等机氯农药通过生成大量的 ROS,可明显激活 ERK1/2 通路,激活的 ERK 通过磷酸化抗凋亡分子,同时激活转录因子,以刺激表达存活相关基因而产生抗凋亡作用^[63]。

已有研究表明,硫丹可诱导斑马鱼^[64]和草鱼(*Ctenopharyngodon idellus*)^[65]肝脏 I 相(APND; ERND)和 II 相(GST)解毒酶活性升高,进而影响正常

生理机能。硫丹暴露可诱导水苳草(*Myriophyllum quitense*)^[66]、大型蚤(*Daphnia magna*)^[30]、虹鳟(*Oncorhynchus mykiss*)^[67]、四眼青鲮(*Jenynsia multidentata*)^[68]、斑马鱼^[45-69]、草鱼^[70-71]、奥尼罗非鱼(*Oreochromis niloticus*)^[72]、中华大蟾蜍(*Bufo bufo*)^[73]、鬼针草蟾(*Bidens laevis*)^[74]、菲律宾蛤仔(*Venerupis philippinarum*)^[75]等水生生物机体产生过量 ROS,并产生氧化胁迫,表现为机体组织 SOD、CAT、GSH-Px、GST 等抗氧化酶活性的非正常变化,LPO 升高,严重导致细胞 NDA 损伤、凋亡、组织病变甚至个体死亡。

2.5 内分泌干扰作用

研究表明硫丹对内分泌系统存在潜在的影响,对人类和生物具有较大的负面影响,其能够干扰生物体内源激素的合成、释放、转运、结合和代谢,从而影响机体的内环境稳定、生殖、发育及行为。体外毒性试验显示,硫丹可以激活雌激素受体 α (ER α)的 AF2 功能,使孕酮受体(PR)水平升高和雌激素响应基层细胞增殖^[76]。通过对 ER α 转染 HeLa 细胞系研究发现,硫丹与雌二醇竞争结合 ER α ,并可反馈激活 ER α ,诱导 ERE 依赖基因表达^[77]。研究表明,硫丹暴露可下调胡子鲶(*Clarias batrachus*)卵巢泛素与 Esco2 蛋白表达,上调黑素皮质素受体-2 蛋白表达^[78];2.5 $\mu\text{g}\cdot\text{L}^{-1}$ 硫丹与 33 $\mu\text{g}\cdot\text{L}^{-1}$ 氟他胺共同影响下,幼体胡子鲶睾丸发育相关转录因子(dmrt1、sox9a、wt1)、类固醇生成酶(11-hsd2、17-hsd12、P450c17)、类固醇激素合成急性调节蛋白、孤核受体(nr2c1、Ad4BP/SF-1)基因表达量显著降低^[79]。硫丹是一种类雌激素,可模拟雌激素的生理作用促进子宫正常发育^[80]。硫丹对鱼类也有类雌激素作用,硫丹暴露可诱导斑马鱼胚胎及幼体卵黄蛋白原(VTG)表达^[81]。对大西洋鲑(*Salmo salar*)肝细胞卵透明带(ZP)和 VTG 基因表达研究^[82]也有类似作用。正常情况下,只有性成熟的雌性动物卵子发生阶段在雌二醇的控制下才能产生 ZP 和 VTG。雄鱼体内含有 VTG 后,雄性特征会逐步退化,雌性特征会逐步明显,雄鱼逐渐雌性化。

甲状腺是动物重要的内分泌器官,其分泌的甲状腺激素 T3、T4 具有重要的生理功能:促进组织分化、生长与发育,作用于细胞核受体,刺激 DNA 转录过程,促进 mRNA 形成,加速蛋白质与各种酶生成,增强碳水化合物利用,促进脂肪酸及脂肪合成等。鱼类甲状腺素对代谢活动、生长、渗透压调节、

生殖、体色、中枢神经活动和行为等方面都有影响^[83]。某些有机氯农药可直接与甲状腺激素受体结合,激活受体或抑制受体,使激素不能发挥正常功能。研究显示,硫丹可影响鱼类的甲状腺激素水平。 $0.1 \mu\text{g} \cdot \text{L}^{-1}$ 硫丹暴露 35 d, 尼罗罗非鱼(*Oreochromis niloticus*)血浆 T4 水平显著降低, T3 水平变化不明显^[84]。同样研究表明,硫丹可不同程度影响萨罗罗非鱼(*Sarotherodon mossambicus*)血清 T3、T4 水平^[85]。有研究显示,硫丹是通过干扰肝脏 I 型脱碘酶和 III 型脱碘酶活性来影响甲状腺激素水平^[86]。鱼类血浆 T3 的浓度与肾脏、肝脏中脱碘酶的活性密切相关^[87]。此外,硫丹还可引起鱼类催乳激素、皮质醇、胰岛素水平变化,从而间接影响鱼类渗透压调节、应激反应及碳水化合物代谢等功能^[85]。

3 总结与展望

本文总结了近年来硫丹的环境分布,并介绍了其对水生生物的毒性及致毒机制。由于硫丹与环境的相互作用复杂,已有的研究结果和认识还存在一定的局限性,因此有必要进一步加强硫丹对水生生物整个生命周期及在多种环境污染物共存条件下硫丹对水生生物的生理生化及生态学研究。另外,应进一步深入研究硫丹污染胁迫下,特别是低剂量长期暴露下,生物体内生理生化反应及分子机制,对于进一步揭示硫丹生物毒性的分子和细胞作用机制及其与机体健康的内在联系具有重要的意义。

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