二氯喹啉酸在稻田水、土壤和作物中残留动态研究*

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摘要 二氯喹啉酸为高效、低毒新型除草剂。在天津和吉林2年2地水田残留实验结果表明，此药在田水和茎叶中消解很快。二氯喹啉酸在田水中的半衰期分别为0.8 d(天津)和2 d(吉林)。在茎叶中的半衰期小于1 d。该农药在土壤中残留较低，消解较快，半衰期约为6 d；在土壤中均未检出二氯喹啉酸代谢物。按推荐剂量421.5—525 g/hm²，施药1次，施药间隔期为96—105 d，糙米中二氯喹啉酸残留量均小于0.005 mg/kg，远远低于最高残留限量，对人是安全的。

关键词 二氯喹啉酸代谢物，消解动态，最终残留，稻田水，土壤，作物。

二氯喹啉酸，通用名Quinclorac (3，7-二氯-8-喹啉羧酸)，为我国正在开发的水田除草剂。主要用于防治稻田中稗草和其它禾本科杂草，具有良好除草效果和较长残效期[1]，施用1次可防除整个生长期的杂草。

为评价这一新型除草剂的环境安全性，为注册登记和推广使用提供可靠数据，于1993—1994年，在天津、吉林2地进行2年田间实验，探索和改进了残留分析方法，考查了二氯喹啉酸在稻田水、茎叶和土壤中残留消解动态，检测了稻杆、稻壳、糙米和土壤中的最终残留量。

1 田间设计与采样

(1) 供试药剂 50%二氯喹啉酸可湿性粉剂，沈阳化工研究院提供。

(2) 田间实验设计 见表1。

表1 实验设计(1993—1994)

项 目	天津市郊杨柳青农场	吉林省农科院水稻所(公主岭市)
水稻品种	1187#	超产1号
小区面积(m²)	20	15
重复次数	3	3
施药量(g/hm² 制剂)	55(A、B、C)，70(D、E、F)	55(A、B、C)，70(D、E、F)
土壤类型	粉砂壤土[1)]	壤粘土[1)]
土壤有机质(%)	2.08[1)]	1.12[1)]
pH值	8.2[1)]	7.3[1)]
插秧日期	1993-06-03 1994-05-23	1993-05-24 1994-05-22
施药日期	1993-06-20 1994-06-24	1993-06-11 1994-06-12
施药方法	兑水，用背俯式喷雾器喷洒	兑水，用背俯式喷雾器喷洒
施药次数	1次	1次
收获日期	1993-10-04 1994-10-06	1993-09-28 1994-09-15

1) 由天津市农科院土壤肥料研究所分析

(3) 残留动态样品 在对照区和高剂量D、E、F处理区，于施药前、施药当天1、2、6 h及

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施药后1、2、4、8、16、30 d分别按对角线方法取水、茎叶及湿泥样(0—5 cm)，混匀、缩分、冷藏(−18℃)、待分析。

(4) 最终残留样品 在对照区、常量A、B、C处理区、高剂量D、E、F处理区，于收获前1 d分别按对角线方法取土壤、作物样品，晾干、缩分、脱粒后待分析。

2 分析方法

2.1 仪器及操作条件

(1) 高效液相色谱仪(HPLC) 美国Waters model 510型，配有紫外吸收检定器。Φ3.9 mm×250 mm不锈钢柱，内填10 μm C_{18}键合砖，流动相为甲醇：1%乙酸水溶液(45/55，*V*/*V*)，流量1 ml/min，检测波长为240 nm，外标法峰高定量检测。

(2) 气相色谱仪(GC) 美国惠普公司，HP-5890-Ⅱ型，配有3396-B型积分仪，ECD检定器，Ultral型毛细管柱(25 m×0.32 m×0.52 μm)，高纯氮为载气，流量60 ml/min，柱头压80 kPa，分流比10∶1，进样口、柱温、检测器温度分别为230℃、230℃、260℃；外标峰面积定量。

2.2 检测项目

水、糙米、稻壳和茎叶(稻杆)中二氯喹啉酸残留量；土壤中二氯喹啉酸及代谢物(3-氯-8-喹啉酸)残留量。

2.3 样品分析

(1) 田水样 0.45 μm微孔滤膜过滤后，直接用HPLC[2]测定。

(2) 土壤样 pH10硼砂缓冲液浸泡、振荡、高速离心，取上清液过0.45 μm滤膜，HPLC测定[3]。若样品浓度过低，将上述上清液用C_8键合硅柱萃取，乙酸乙酯洗脱[2]、重氯化[4]，GC-ECD测定。

(3) 糙米、稻壳、茎叶(稻杆)样 先后用碱液和丙酮浸泡、CH_2Cl_2萃取、浓缩、硅胶柱净化[5]、重氮化[4]、氮吹至干，用己烷/丙酮(1∶1)定容，GC-ECD测定。

(4) 添加回收率 高效液相色谱方法：田水样、土壤样中二氯喹啉酸添加平均回收率为80.9%—100.3%；变异系数为0.3%—4.4%。土壤样中代谢物添加平均回收率为87.2%—91.7%，变异系数为2.6%—4.4%。气相色谱方法：土壤样、作物(茎叶、稻壳、糙米)样中二氯喹啉酸添加平均回收率为82.8%—99.2%，变异系数为1.4%—8.0%；土壤代谢物回收率为75.7%—85.1%，变异系数为6.3%—7.1%。

(5) 方法最低检出浓度 二氯喹啉酸在田水中为0.002 mg/kg(HPLC法)；在糙米、稻壳、茎叶(稻杆)中0.005 mg/kg(GC法)；在土壤中为0.005 mg/kg(HPLC法)、0.001 mg/kg(GC法)。代谢物在土壤中为0.010 mg/kg(HPLC法)和0.005 mg/kg(GC法)。

3 结果与讨论

3.1 二氯喹啉酸在田间的消解动态

(1) 二氯喹啉酸在稻田水中消解动态见图1。天津、吉林2地实验结果表明，施药6 h后，二氯喹啉酸在水中的残留量达到最高值。在天津D、E、F处理区分别为0.740、0.910、0.740 mg/kg，第1 d平均消解率为63.9%；8 d消解率>97%，16 d残留量低于检测限；半衰期为0.8 d。吉林实验区施药6 h后，D、E、F处理区二氯喹啉酸在水中的残留量分析为0.684、0.757、0.612 mg/kg，第1 d消解率为30.7%，8 d消解率>97%，30 d未检出；半衰期2 d。可见该农药在天津、吉林稻田水中消解都比较快，2地相比，在天津田水中消解更快。

(2) 二氯喹啉酸及代谢物在土壤(湿泥)中消解动态见图1。天津实验地施药第1 d，二氯喹啉酸在土壤中的残留量达最高值，D、E、F处理区分别为0.023、0.016、0.031 mg/kg，第8 d残留量降至检测限以下；在吉林施药后第2 d达最高值，D、E、F处理区依次为0.121、0.159、0.140 mg/kg，第30 d残留量为0.010 mg/kg。半衰期为6 d，均未检出代谢物。天津、吉林2地实验结果比较表明，在土壤中，天津较吉林残留量低且消解快，土壤质地差异是其

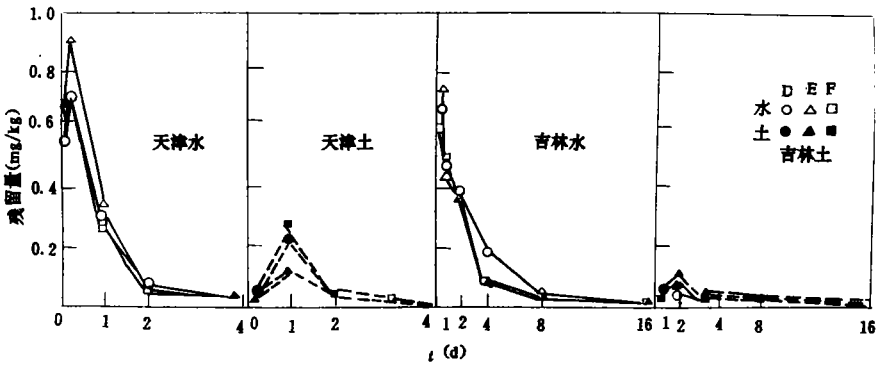

图 1　二氯喹啉酸在稻田水、土中的残留动态(1993 年)

主要原因。天津为粉砂壤土，质地较疏松(物理性粘粒＜0.001 mm 为 16%)，透水性强、土壤 pH 值较高，二氯喹啉酸在水中溶解度较大，随着田水的淋溶，水和土壤中残留消解都较快，土壤中残留量较低；吉林为壤粘土，质地密(物理性粘粒＜0.001 mm 为 26%)、pH 值较低，土壤中残留量较高，水和土壤中残留消解亦比天津慢。

(3) 二氯喹啉酸在处理区相邻稻田及支渠水、土中残留状况　二氯喹啉酸在水田环境中的归趋国外研究发现[6]，此药比较稳定，不易挥发、水解及微生物降解；光解及土壤吸附过程也较微弱。该药水中溶解度较大(64 mg/L，20℃)，且随着田水和土壤 pH 增高，其水中溶解度迅速增加。在美国加州室内和田间研究已发现，此药可随田水在水层和土壤层中产生水平和纵向移动，移动程度与土壤性质有关[7]。为考查这一情况，在实验地，对与处理区相邻稻田和灌溉支渠水、土壤进行了监测。从表 2 可见，天津和吉林实验地处理区相邻的稻田水中未检出二氯喹啉酸，而在土壤里检测出 0.006—0.023 mg/kg 二氯喹啉酸。灌溉支渠水中残留量为 0.004—0.032 mg/kg，土壤中为0.008—0.019 mg/kg，表明二氯喹啉酸在水和土壤中有水平移动现象。为防止对地表水及地下水造成污染，应对二氯喹啉酸在不同水质和土质条件下的水平和纵向移动作进一步研究和探讨。

(4) 二氯喹啉酸在水稻茎叶上消解动态见图 2。该药在水稻茎叶中消解亦很快。天津、吉林 2 地，施药 2 d 后茎叶中残留消解率均在 80%以上，半衰期均小于 1 d。施药 1 h 残留量达最高值。天津 D、E、F 3 个区分别为 4.581、4.476、3.106 mg/kg；吉林分别为 1.506、1.938、1.056 mg/kg，天津约为吉林实验区残留量的 3 倍，这是由于施药时天津实验地苗大叶茂，吉林实验地气温偏低(较天津同期平均气温低 10℃)，苗小叶少，因此，2 地茎叶上农药的原始附着量有很大差异。

表 2　二氯喹啉酸在处理区相邻稻田及支渠中残留状况(mg/kg)

采样距施药时间(d)	天津				吉林			
	邻区		支渠		邻区		支渠	
	田水	土壤	田水	土壤	田水	土壤	田水	土壤
1	ND	0.012	0.004	0.019	ND	ND	0.010	ND
2	ND	0.012	0.007	0.008	ND	0.006	0.032	0.009
4	ND	ND	ND	ND	ND	0.023	0.014	ND
8					ND	0.016	ND	ND

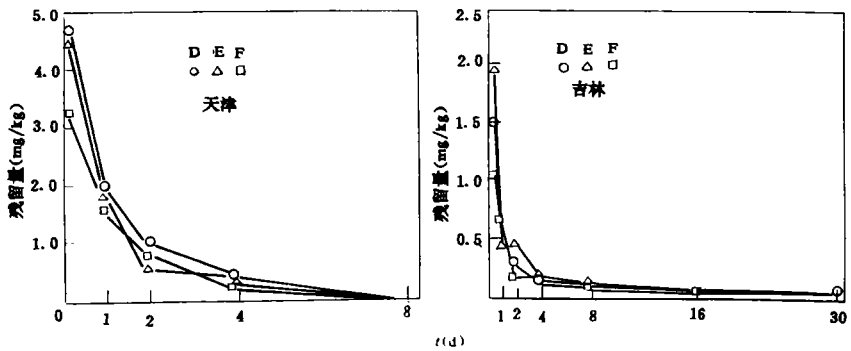

图 2 二氯喹啉酸在水稻茎叶中残留动态(1993)

3.2 二氯喹啉酸及代谢物最终残留量

1993、1994 年 2 年，天津实验地施药到收获间隔期为 105—107 d。常量处理区糙米、稻壳、稻杆样均未检出二氯喹啉酸残留(<0.005 mg/kg)。1993 年高剂量处理区 D、E、F 稻杆样中检出二氯喹啉酸残留分别为 0.005、0.010、0.008 mg/kg，D 区稻壳样残留为 0.021 mg/kg，其余未检出。吉林实验地 1993、1994 年 2 年，施药到收获间隔期为 96—109 d，常量处理区均未检出，仅 1994 年高剂量处理区 F 稻壳样中检出二氯喹啉酸残留为 0.013 mg/kg，其余未检出，2 年 2 地实验中，土壤样品均未检出二氯喹啉酸及代谢物(二氯喹啉酸残留<0.001 mg/kg；代谢物残留<0.005 mg/kg)。

4 小结

(1) 本研究采用先进的残留分析方法。样品预处理用微孔滤膜和 C_8 键合硅柱固相萃取手段，高效液相色谱和毛细管气谱检测，此方法步骤简单，回收率高，灵敏准确，提供了可靠的分析数据。

(2) 据日本环境保护研究所资料介绍，该药在水稻糙米中最高允许残留量为 0.5 mg/kg。2 年 2 地最终残留结果表明，无论常量及高剂量处理区，二氯喹啉酸在糙米中残留量均低于检出限，即<0.005 mg/kg，远远低于最高允许限量。常量处理区稻壳、稻杆中二氯喹啉酸残留量亦小于 0.005 mg/kg，高剂量处理区仅个别区稻壳、稻杆中检出残留 0.005—0.021 mg/kg，浓度也是很低的。其余均低于 0.005 mg/kg。由此得出：按推荐剂量 825—1050 g/hm^2，施药 1 次，施药后 105 d(天津)或 96 d(吉林)收割水稻对人是安全的。

(3) 二氯喹啉酸在田水、土壤及茎叶中，持留时间短，且低毒、高效，是一种有发展前途的新型水田除草剂。

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that PCP removal by granular sludge in UAD reactors was due to biodegradation rather than adsorption and volatilizaiton.

Key words: pentachloropenol, biosorption, de-sorption, biodegradation, anaerobic.

Photocatalytic Oxidation of Benzene Hexachloride and Pentachlorophenol in Aqueous Solution. Li Tian and Qiu Yanling (School of Environ. Eng., Tongji Univ., Shanghai 200092): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 24—26

Photocatalytic oxidation of low concentration of benzene hexachloride (BHC) and pentachlorophenol (PCP) in aqueous solution is studied with a high pressure mercury lamp as radiation resource and TiO_2 as a catalyst. BHC can be oxidized easily, half life periods of the 4 isomers of BHC are all around 20 minutes. Oxidation rate of γ-BHC is higher under neutral condition. Chlorinated medium products formed in the photocatalytic oxidation of BHC can be gradually removed by further reaction. For PCP reaction rate of photocatalytic oxidation is much higher than that of photolysis. Dechlorination of PCP can be completed within 30 minutes. As the reaction process continues, PCP will be oxidized into simple small molecules and finally mineralized completely. It is predicable that photocatalytic oxidation has bright prospect in advanced treatment of drinking water.

Key words: photocatalytic oxidation, benzene hexachloride, pentachlorophenol, aqueous solution.

The Dissipation and Residue of Quinclorac in Rice Field Water, Soil and Rice Plant. Wang Yiru et al. (Institute of Agro-environmental Protection, Tianjin 300191): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 27—30

Quinclorac is a new herbicide with high efficiency and low toxicity. The field experiments were carried out both in Tianjin and Jilin Province in 1993 and 1994, respectively. It has been found that the herbicide dissipated rapidly from water and leaves. Its half life values in the water was 0.8 days in Tianjin and 2 days in Jilin, and the half life in rice leaves was less than 1 day. The residure in sediment remained quite low during 6 days of half life. No metabolite was detected in soil. Applied to rice field as a 50% WP formulation at the recommended rates of 412.5 g—525 g/hm^2, one application, preharvest interval 96—105 days, the residue remaining in unpolished rice was less than 0.005 mg/kg, far below MRL, and was safe to humanbeing.

Key words: Quinclorac, metabolite, dissipation, final residue, water, rice, soil.

Wet Air Oxidation Treatment of H-acid Production Waste Liquor. Wang Yongyi et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 31—33

Under the condition of reaction temperatures of 200—250℃, initial oxygen partial pressures of 1—3 MPa, the wet air oxidation (WAO) of H-acid has 2-step process, including rapid reaction step, in which during the first 10 minutes after the beginning of the reaction COD is decreased rapidly, and UV/Vis. absorbance is increased drastically at first and then reduced rapidly, and slow reaction step, in which, both COD and UV/Vis. absorbance are decreased slowly during about 20 minutes. WAO treatment can improve biodegradability of H-acid significantly. After 1 hour reaction carried out at 160℃ and 3 MPa initial oxygen pressure, COD was decreased by 50%, and the BOD_5/COD ratio of 10 g/L H-acid solution was increased from 3.4% to 33.3%. The offgas from the WAO treatment of H-acid contains undetectable amount of SO_2 and nitrogen oxides.

Key words: wet air oxidation, H-acid, biodegradability.

Emission Factors of Trace OCS from Crop Residues Burning and Estimation Its Amount in China. Cao Meiqiu and Zhuang Yahui (Research Center for Eco-Environmental Sciences, CAS, Beijing 100085): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 34—36

A method of sampling and analysis for trace carbonyl sulfide has been described. The sample is trapped and concentrated at temperature of liquid N_2 and liberated directly into a gas chromatographic column. The concentration of OCS in compressed air as determined as 2.94×10^{-3} μg/L. The method accuracy expressed in term of standard deviation coefficient is ±0.72%. The emission factors of carbonyl sulfide, which were measured during the combustion of rice straws, maize stalks and wheat stalks in an enclosed combustion system, are 1.80, 2.75 and 2.05 g/t for rice straws, maize stalks, and wheat stalks, individual. Standard deviation coefficient are ±6.67%, ±8.36%, and 9.27% for rice straws, maize stalks, and wheat stalks, respectively. Distribution of the amount of crop residues burned in China is presented with a resolution 1° latitude × 1° longitude. The amount of trace OCS could be calculated with their emission factors.

Key words: carbonyl sulfide, biomass buring, emission factor.

The Study of Trace Elements in Human Hair from the Area of Endemic Arsenism. Jiang Ling et al. (Institute of Environ. Medicine, Tongji Medical Univ., Wuhan 430030): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 37—39

217 hair samples and environmental samples from endemic arsenism in Linhe, Inner Mongolia were analyzed. The results showed that the levels of As, Cu and K in hair in studied area were higher than that in control area, but Zn and Se was opposite. The relationship between the typical symptoms of arsenism and the levels of As, Cu, K and Se in hair were found. There were rank correlations between the concentration of Se, Zn, Cu in hair and As in hair (the coefficient = −0.988, −0.794, 0.783, respectively).

Key words: endemic arsenism, trace elements, hair.

Research for the Problem about the Environmental Discount Rate. Wang Yonghang and Fu Guowei (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 40—43

This paper presents a new formula, which describes the relation between private rate or return and social rate of return. The formula includes two environmental parameters, λ, the fraction of national income spent on environmental investment, and η, the elasticity of environmental improvement with respect to environmental spending. From the formula it can be seen that social rate of return or environmental discount rate should decline systematically over time from the point of view of environmental