杀虫双在土壤中的动态研究

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摘要 本文参照 OECD (经济合作与发展组织)的标准,以室内模拟条件,对杀虫双在土壤中的动态进行了淋溶试验. 结果表明,杀虫双淋溶性极强,土壤中绝大部分杀虫双可被水淋溶,留在土壤中的也可随着水的不断加入而被淋溶出. 土壤性质对淋溶影响很小,而流速、温度对淋溶影响较大.

关键词 杀虫双,淋溶,土壤.

杀虫双(2-N, N-二甲胺基-1,3-双硫代硫酸钠丙烷)是我国七十年代自己研制的一种新农药,由于它对水稻、麦类和蔬菜等作物的害虫有良好的防效和杀虫谱广等特点,广泛施用于我国农田虫害的防治. 杀虫双易溶于水,长期施用能否造成对土壤环境和地下水的污染,需要研究其在土壤环境中的物理化学行为. 本文就杀虫双在不同土壤中的动态进行了淋溶试验.

常见的淋溶有柱法[1]和土层色谱法[2]两种,本实验选用了柱法,按 OECD 的试验准则,对我国四种不同类型的土壤进行了室内模拟试验.

一、材料与方法

1. 供试土壤

黑龙江北安县土,河南封丘县潮土,江苏江宁黄棕壤,江西鹰潭红壤. 理化性质见表 1.

表 1　供试土壤理化性质

土壤	采样点	pH (水:土 1:1)	有机质含量 (%)	阳离子交换量 (cmol/kg)	机械组成(%)			质地
					砂粒 (0.02—0.2mm)	粉砂粒 (0.002—0.02 mm)	粘粒 (<0.02mm)	
黑土	黑龙江北安县	5.54	6.50	338.2	28.0	38.9	33.1	壤粘土
潮土	河南封丘县	8.25	0.65	59.8	51.1	31.0	17.9	粘壤土
黄棕壤	江苏江宁县	7.03	1.53	174.2	35.0	38.3	26.7	粘壤土
红壤	江西鹰潭	4.85	1.16	98.2	26.0	32.6	41.4	粘壤土

2. 杀虫双

贵州省化工研究所提供,含量 99.5%.

3. 淋溶柱

参照 OECD 标准,内径 5cm、长 35cm 的聚乙烯塑料管,共分三节,最上端一节为 15cm (5cm 是容水的),其它两节各为 10cm,节与节间用法兰加垫圈,并用螺丝固定。最下端呈漏斗状,下接橡胶导管和流量控制夹,以及淋溶水承受器。

4. 装柱

将 35 cm 长的淋溶柱连接好,在柱下端的漏斗内出口处放一层玻璃棉,装入洗净的石英砂,再覆盖一层玻璃棉,然后将过 18 号筛孔(孔径 1mm)的供试土均匀地装入柱内 (边装边敲柱外壁,使之装实.)填入土量视土壤容重而定,潮土、红壤和黄棕壤三种土壤入量均为 800g,

收稿日期: 1992 年 1 月 7 日

黑土有机质含量高，容重低，装柱量为 650g，以虹吸的方式从土柱底进水，使土壤水分达到饱和，备淋溶试验用.

5. 淋溶试验

从土柱顶先加入 16ml 100mg/L 的杀虫双溶液，上面覆以 1cm 土层，然后从柱顶陆续加水，控制流速，在 24 小时左右结束. 注意使柱顶经常保持 30—50mm 水层，使水面不低于土壤. 淋溶试验开始，分次定量(每次约 40ml)收集淋溶水，直至无淋溶水滴出为止，并测定淋溶水和不同层次土壤中杀虫双的含量.

6. 淋溶水样处理

吸 10ml 淋溶水于 25ml 容量瓶中，用 40% NaOH 将 pH 调至 8.5—9.0，加 2ml 0.2mol Na_2S，放 70℃ 水浴中 2.5 小时，用乙醚萃取，萃取液备气相色谱测定.

7. 土壤样品处理

每 5cm 采样 30g，重复 2 个，在盛有 30g 土样的离心管中加 30ml 蒸馏水，4 滴 0.5mol 的 HCl，用玻璃棒搅匀，机械震荡半小时，在 5000 转/min 下离心 5min，吸取上清滤液 10 ml 于 25ml 容量瓶中，下面处理和水样处理相同.

8. 色谱条件

日本岛津 GC-9A，带有 ^{63}Ni 电子捕获检测器，固定相为 10% OV-225，担体为 Chromosorb W80-100 目，色谱柱为内径 2mm × 2m-玻璃柱. 柱温 160℃，进样器温度 250℃，检定器温度 250℃，载气为高纯氮(99.99%)，流速 40ml/min.

二、结果与讨论

1. 杀虫双在淋溶水中的分布

(1) 土壤性质对淋溶的影响 一般淋溶研究，只是求出淋溶水总体积中农药的量. 为了解杀虫双随水下移的变化及其在水中的分布状况，在恒定的流速淋溶过程中定量接收淋溶水，并根据流速和体积求出杀虫双透过土柱的时间，由时间差异来判断土壤性质对淋溶的影响. 在流速为 10—20ml/h 时杀虫双透过潮土约 8 小时、黄棕壤 8—13 小时、红壤 7—13 小时，黑土 4 小时左右. 显而易见，杀虫双透过土壤的先后顺序是黑土、潮土、黄棕壤和红壤. 按先后次序收集的淋溶水及杀虫双含量列于表 2，从表中的结果可见，最先淋出水中无杀虫双检出，这部分水只是加杀虫双前柱中的饱和水. 说明杀虫双在淋溶水的带动下，通过 30 cm 的土柱，还需一定时间，所需时间的长短和淋溶出的药量可证实土壤理化性质对淋溶的影响.

表 2 杀虫双在淋溶水中的分布 (mg/L)

水 / 温度(℃) / 序号	潮土(水)		黄棕壤(水)		红壤(水)		黑土(水)	
	30	4	30	10	30	6	30	15
1	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0
3	0.16	0.91	0	0	0	0	0.02	0.02
4	1.23	1.22	0	0	0.10	0.12	0.24	0.03
5	2.43	1.00	0.77	0.44	0.60	0.64	0.73	0.04
6		0.98	1.14	0.79	1.10	0.64	1.28	0.60
7		0.85	1.35	0.36	0.95	0.85		1.00
8		0.78		0.27		0.62		1.26
9		0.69		0.27		0.49		0.78
10				0.17		0.34		0.54
11								0.54

(2) 流速和淋溶水加入量的影响 流速和淋溶水的加入量也直接影响杀虫双的动态与分布. ① 潮土在加水量相同情况下，流速高、接

收淋溶水次数少的淋溶水中杀虫双含量从无到有，从低到高．而在流速低、接收次数多的淋溶水中，杀虫双含量是从无到有，从低到高，再从高到低．② 黑土在流速相同、加水量少接收次数少和水量多接收次数多的情况下，杀虫双在淋溶水中的含量也有类似的结果(见图1)．这反映出，尽管杀虫双淋溶性很强，但在土壤中仍经受吸附、解吸和分配再分配的交替作用．只是在流速快、时间短时，这些作用显示很弱，致使杀虫双很快随水被淋溶出来，其浓度随淋溶水的接收次数而增加，相关系数达显著和极显著水平．

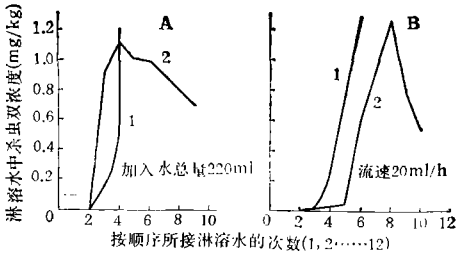

图1　杀虫双在淋溶水中的动态变化曲线

A 潮土(1.流速 12ml/h, 2.流速 4.7ml/h)
B 黑土(1.加入总水量 250ml, 2.加入总水量 460ml)

2. 杀虫双在土壤中的分布

潮土、黄棕壤和红壤的装柱量均为 800g，加入杀虫双 1600μg，土壤中杀虫双浓度为 2 mg/kg；黑土有机质含量高、容重低、装柱量为 650g，加入杀虫双 1600μg，土壤浓度为 2.5mg/kg；加水量 220—460ml，相当 102—234mm 的降雨量．杀虫双易淋溶，能较快透过土柱，所以在四种土壤中的残留量相对较低．在土壤间、土壤各层次中杀虫双的分布有差异(见表 3)．在潮土和黄棕壤中的杀虫双主要集中在 20—25cm 层，其中的含量分别占土壤总含量的 52%、44%．红壤主要集中在 5—15cm 层，其中的量占土壤总含量的 58%．从而可看出，潮土和黄棕壤中的杀虫双吸附性小，易于下移，待淋溶后，0—15cm 的土层中已测不出杀虫双．红壤 0—25cm 土层含杀虫双，而 25—30cm 的土层中测不出．黑土 0—5 cm 土层中测不出，5—30cm 层测出，含量趋向于上层低、中间高、底层低．

表3　杀虫双在土壤各层中的分布 (mg/kg)

土层深度 (cm)	潮　土		黄棕壤		红　壤		黑　土	
	30℃	4℃	30℃	10℃	30℃	6℃	30℃	15℃
0—5	0	0	0	0	0.020	0	0	0.010
5—10	0	0	0	0	0.250	0.070	0.120	0.010
10—15	0	0	0	0	0.210	0.170	0.270	0.020
15—20	0.410	0	0.175	1.190	0.170	0.050	0.470	0.020
20—25	0.660	0.115	0.710	0.800	0.190	0.010	0.470	0.040
25—30	0.210	0.125	0.125	0.350	0	0	0.730	0.080

3. 杀虫双在淋溶水中的量及土壤性质、温度对淋溶的影响

(1) 杀虫双在淋溶水中的量　从表 4 可看出，任何一种土壤，淋溶水中杀虫双的回收率都高于土壤回收率 20% 左右，即 70% 左右的杀虫双在淋溶水中．说明土壤对杀虫双的吸附很弱，如继续增加水量或加长土柱，杀虫双仍可被淋溶或继续下渗．

(2) 土壤性质的影响　四种土壤，黑土有机质含量最高，达6.5%．粘粒含量 33.1%，对杀虫双的吸附能力应是较强的，但从表 4 数据看，土壤中杀虫双的量是很少的，仅占水土总回收量的 20% 左右．说明有机质对杀虫双的吸附也是很弱的，再则，因高有机质含量的土壤，一般都是带负电荷，对带相同电荷的杀虫双是排拆的，少量吸附也是靠范德华力和静力的作用．而这种作用又不断受到淋溶水的影响，使被吸附的杀虫双又解吸出来．甚至吸附还未达到平衡，就在淋溶水的带动下下移．加之有机质含量高的土壤松软，透水性好，以致 80% 的杀虫双分布在淋溶水中．

表 4 淋溶水、土壤中杀虫双的回收率(%)

土壤 / 温度(℃) / 样	潮土		黄棕壤		红壤		黑土	
	30	4	30	10	30	6	30	15
水	61.0	50.0	39.5	32.2	34.5	48.0	66.0	61.1
土	10.8	14.4	11.8	8.7	46.9	17.9	17.0	9.3
水+土	71.8	64.4	51.3	40.9	81.4	65.9	83.0	70.4

(3) 温度的影响 升高温度可加速土壤中化合物的理化反应，为探讨温度对杀虫双淋溶的影响，分别在高温和低温下做了对比试验.从表 4 结果说明，升高温度不仅可提高水中杀虫双的回收率，而且可显著提高土壤中杀虫双的回收率，视土壤性质的不同，提高的幅度不一样. 其中水中的回收率可提高 20% 左右，土壤可提高 35—160%. 可能是温度升高增加了水中杀虫双的溶解度，降低了水的粘滞度和张力，从而加速了杀虫双的淋溶速度，增加了淋出量.

杀虫双的移动深度不受加入到土壤表面量限制，加入的量减半也可下移到同等深度.加入量的多少，只是在土壤、水回收率中和土壤不同层次间的浓度中有差异，加入的量越大，回收的量就越多，不同层次中的浓度就越高.

综上所述，杀虫双的淋溶受土壤性质的影响较小. 在供试土壤中，不管是有机质、pH、还是粘粒含量和阳离子交换量，都未显著影响杀虫双的淋溶. 所以在施用量大，面广和雨水多的地区，要特别注意杀虫双对地下水的污染问题.

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量有困难，而酶免疫分析则可选择使用的方法.

由于公众对环境质量的要求日益强烈，而常规方法费用高、时间长，受仪器和分析能力限止，因此酶免疫分析将会得到更快的发展.

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well as the operation conditions of the pond.

Key words: waste water, stabilization pond, anaerobic, biodegradation, benthic deposit.

Synthesis of 1-Hydroxypyrene and Its Identification. Ma Jiang zhao (Beijing Municipal Research Institute of Environmental Protection, Beijing 100037): *Chin. J. Environ. Sci.*, **13**(4), 1992, pp.27—30

A procedure for the preparation of 1-hydroxypyrene from pyrene was described. Its mass spectrum, nuclear magnetic resonance, infrared, ultraviolet and fluorescence spectra were determined. The results show that the compound thus prepared is a very pure product.

Key words: 1-hydroxypyrene, pyrene.

Research on Leaching Dynamics of Dimethypo in Soils. Li Deping, Jin wei (Institute of Soil Science, Academia Sinica, Nanjing 210008) *Chin. J. Environ. Sci.*, **13**(4), 1992, pp.31—34

With reference to OECD-Chemicals Testing Guidelines, laboratory experiments were carried out to examine the leaching dynamics of dimethypo in soils. The results suggest that dimethypo possesses a strong tendency of leaching. Thus, most of the pesticide can leach through the soil columns. With the continuous addition of leaching water, all the pesticide in soil columns can leach out. Soil properties did not show great influence on leaching, while flow rate and temperature exerted remarkable effect on leaching dynamics of dimethypo.

Key words: dimethypo, leaching test, dynamics.

Study on the Degradation of Hydrazine Hydrate in River Water. Sun Hong et al. (Environmental Protection Monitoring Station of Benxi 118000):*Chin. J. Environ. Sci.*, **13**(4), 1992, pp. 35—39

Labo ratory studies and monitoring practice in a river demonstrate that the degradation of hydrazine hydrate can be described by the first-order reaction dynamics. Its degradation rate was found to be dependent on water temperature, microorganism, concentration of dissolved oxygen, pH and other conditions. The effect of temperature on the degradation rate could be expressed with the formula: $K_T = K_{20} \cdot \theta^{(T-20)}$ Calculation with computer shows that when pH=6, then $K_{20} = 0.028\ 1/h$ and $\theta = 1.045$, when pH = 8, then $K_{20} = 0.021\ 1/h$, $\theta = 1.036$. The degradation coefficient of hydrazine hydrate measured in the experiment carried out in the river was equal to 0.3001/h.

Key words: hydrazine hydrate, degradation, first-order reastion dynamies

Oxidation Dephenolization of Waste Water Catalyzed by Horseradish Peroxidase Hu Longxing et al. (Shanghai University of Technology 200072): *Chin. J. Environ. Sci.*, **13**(4), 1992, pp 40—44

The results of the study on oxidation dephenolization of waste water catalyzed by horseradish peroxidase show that for the treatment of waste waters containing only one of the three phenols (phenol,o-chlorophenol and o-aminophenol), the highest pheanol removal efficiency can be reached at pH values around 7. It was also found that at low (4°C) and high (40°C) temperatures, the removal efficiencies reduced by about 10%, and in the treatment of waste water containing more than one phenols, there existed synergistic effect among various phenols resulting in phenol removal efficiencies as high as 95%.

Key words: phenols, waste water treatment, horseradish peroxidase.

A Study on Modification of the Surface of Coal Ash. Lü Yaojiao, Zhang Jishuang (Hunan University 410082): *Chin. J. Environ. Sci.*, **13**(4) 1992, pp.45—47

The modification of the surface of coal ash was achieved by treating the ash with six kinds of surfactants including H-NA, H-R through dry or wet processes of activation. Experiment results indicate that the number of hydroxyl group on the ash surface decreased while corresponding groups of activator increased resulting in the improvement of its property of dispersion in organic medium. The properties of processed PVC and rubber samples with the activated coal ash as filler were greatly improved compared with those products with untreated ash as filler. All the technical targets of the new products, except for the decrease of abrasive wear of rubber, which needs to be further improved, reached or surpass the relevant standards. No doubt, thtis is a new path for making use of the regenerated resource with the advantages of lowering the cost of composite material and protecting the environment.

Key words: coal ash, surface modification, composite material.

Taxonomic System for Environmental Science. Wang Huijun, Chen Jingsheng (Center of Enviro. nmental Science, Peking University, Beijing 100871): *Chin. J. Environ. Sci.*, **13**(4), 1992, pp. 48—51

A new and more reasonable taxonomic standard for environmental science is introduced based on the systematic anaysis of the synthetic, integrate and inter-disciplinary character of the science and the forms and extent of the synthesis and integration. According to the new standard, environmental science can be regarded as an organic entirety composed of three levels of interrelated discipline groups.

Key words: taxonomic system, environmental science.

Application of Enzyme Immunoassay in Pesticide Analysis Li Zhixiang, et al. (Institute of Agro. environmental Protection Tian Jing 300191): *Chin. J. Environ. Sci.*, **13**(4), 1992, pp. 51—55

This paper introduces briefly the technique of Enzyme Immunoassay and its application in pesticide analysis. The basic types, principles, procedures of development and the prospect of future application and further advancement of Enzyme Immunoassay were discussed.

Key words: pesticides, enzyme immunoassay.

Application of Micronuclues Test in *Vicia Faba* Root Tips in the Rapid Detection of Mutagenic Environmental Pollutants. Ruan Cuicai, Liang Yu. an, Liu Jinling et al. (Guangxi Cancer Institute, Nanning 530027): *Chin. J. Environ. Sci.*, **13**(4), 1992, pp. 56—59

Micronucleus test in vicia faba root tips was performed for