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A Mini Model Ecosystem about the Fate of Labeled Pesticides*

Zhong Chuangguang[1)] Chen Shunhua[1)] Carvalho F P[2)] Zhao Xiaokui[1)]
(1) School of Life Sciences, Zhongshan University, Guangzhou 510275;
2) International Atomic Energy Agency, Marine Environment Laboratory, Monaco)

Abstract A mini model ecosystem inside a vial to study the fate of labeled pesticides was developed. In this new system, the ecosystem was limited in a 3 mL test tube (1 mL water and 0.5 g sediment) with labeled pesticide. Volatile compounds were trapped by polyurethane cotton which was placed above the test tube. $^{14}CO_2$ released from the ecosystem would be absorbed by NaOH in the bottom of the vial. A comparative study of the fate of 9 labeled pesticides, ^{14}C-DDT, ^{14}C-BHC, ^{14}C-chlopyrifos, ^{14}C-trichlorphon, ^{14}C-mono crotophos ^{14}C-fenvalerate, ^{14}C-chlordimeform, ^{14}C-bensulfuron methyl, and ^{14}C-chlorsulfuron, in marine mini model ecosystem was conducted.

Keywords mini model ecosystem, labeled pesticides, fate
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Pesticides or organic compounds in ecosystem may have two major ways of loss, volatilization and biodegradation. Therefore, when studying the fate of pesticides or organic compounds, both volatilization and biodegradation should be considered. The approach used in the previous studies was as described by Kearney et al[1] in which there were not only several separate apartments for the absorption of CO_2 and volatile compound but a model ecosystem as well. With this kind of approach, many valuable data have been obtained. However, since air flow should be used to drive CO_2 and volatile compounds out of the apartment of the model ecosystem, it is doubtful that whether this system could represent aquatic environment, especially the marine one's, because the dissolved oxygen is rather low in typical marine environment. This paper introduces an assembly mini model ecosystem inside a vial to study the fate of labeled pesticides or organic compounds, with which the aforementioned disadvantage can be overcome.

1 Materials and Methods

1.1 Materials

(1) Labeled pesticides: studied pesticides include ^{14}C-DDT, ^{14}C-BHC, ^{14}C-chlopyrifos, ^{14}C-trichlorphon, ^{14}C-fenvalerate, ^{14}C-chlordimeform, ^{14}C-monocrotophos, ^{14}C-bensulfuron methyl, and ^{14}C-chlorsulfuron.

(2) Scintillation cocktail: the cocktail is composed of 6 g of PPO, 500 mL of toluene, 500 mL of Triton X-100, 500 mL of methyl alcohol.

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(3) Liquid scintillation spectrum analyzer: Packard Tri-Carb CA 2000/LL.

1.2 Methods

The mini model ecosystem: the diagram of the mini model ecosystem for the study of the fate of pesticides is shown in Fig 1. All the components of the system are inside a 20 mL vial which is commonly used for detection by liquid scintillation counter. It consists of: ① a 4 cm glass test tube inside which there are 0.5 g of wind dried sediment collected from Daya Bay, 1 mL of sea water and ^{14}C labeled pesticides; ② a glass base for fixing the tube; ③ a paper funnel containing 100 mg polyurethane cotton (cotton covered with polyurethane) to trap the volatile compounds including parent compounds and any volatile degradation products; ④ 0.5 mL NaOH (c= 10%) in the bottom of the vial to absorb the released $^{14}CO_2$ from the ecosystem.

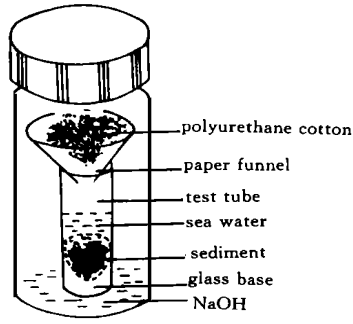

Fig. 1 Diagram of the mini model ecosystem

Experiment began in March with the temperature ranging from 16~25℃. At the end of 1, 2, and 4 weeks, duplicate samples were collected. The tube was withdrawn from the vial, 5 mL of cocktail was added into the vial, and polyurethane cotton was directly put into the vial containing 5 mL of cocktail. The radioactivities of the above samples were counted in Scintillation Spectrum Analyzer. The content in the tube including water and sediment was transferred into a vial, added with 10 mL of cocktail. After more than 10 h, this vial was counted for extractable compounds. Then the sediment was washed by 10 mL methyl alcohol for four times, dried, and the radioactivity of bound compounds was counted by G-M counter. The counts of the sediment was converted to activity which based on the efficiency of the counter.

Due to self-quenching by the compound of chlorpyrifos, the counts of the radioactivity of chlorpyrifos were corrected via dilution.

2 Results and Discussions

The fate of the pesticides was expressed as 3 parameters: volatile, CO_2, and bound, where the volatile was the radioactivity of the polyurethane cotton, CO_2 was the radioactivity in NaOH solution, the bound was that remained in sediment after extraction procedure.

2.1 Volatilization

The volatilization of pesticides was consistent with their vapor pressure (Table 1, 2). Highest volatilization of the pesticides was observed in BHC with 18.80%, 30.29% and 31.78% of the applied radioactivity at the end of 1, 2 and 4 weeks respectively. It was evident that the volatilization was increased with time. This is consistent with data of γ-BHC obtained by other researchers. With a vapor pressure of 5.59×10^{-3} Pa, γ-BHC has been shown to undergo rapid volatilization from tropical ecosystems[2-4]. Higher volatilization was also found in Chlopyrifos with 7.40%, 8.69% and 7.76% of applied radioactivity at the end of 1, 2 and 4 weeks. However, it seemed that volatilization of chlopyrifos occurred in first week and reached equilibrium. The volatilization rates of the other pesticides were below 1%, among which chlorsulfuron and fenvalerate even were 0 (Table 2).

Tab. 1　The vapor pressure of the pesticides (at 20℃)[5]　　Pa

Pesticides	Trichlorphon	BHC	Chlorpyrifos	DDT	bensulfuron methyl	mono crotophos	fenvalerate	chlordimeform
Vapor pressure	9.98×10^{-4}	5.59×10^{-3}	2.49×10^{-3}	2.53×10^{-5}	1.73×10^{-3}	2.93×10^{-4}	2.93×10^{-5} (22℃)	2.93×10^{-5}

2.2 Degradation

The pesticides could be divided into 2 groups of the stable and the unstable one. BHC, DDT, chlopyrifos, chlorsulfuron and bensulfuron methyl are stable pesticides. In this group, only less than 1% of applied radioactivity became CO_2 after 4 weeks of incubation (Table 2). Trichlorphon, mono crotophos, fenvalerate, chlordimeform belong to the unstable group, in which rapid biodegradation was detected. The production of CO_2 was 42.44%, 15.84%, 10.83% and 4.96% for trichlorphon, fenvalerate, mono crotophos and chlordimeform respectively at the end of 1 week. Trichlorphon was the most unstable one among the pesticides studied. The CO_2 production of Trichlorphon was 42.44%, 44.16% and 55.54% respectively at the end of 1, 2 and 4 weeks. The degradation pattern of chlordimeform was different from others. CO_2 was increased evenly and steadily, then reached 31% of the applied radioactivity at the end of 4 weeks. According to the data of 4 weeks, the stability of the second group could be ranked as: mono crotophos, fenvalerate, chlordimeform and trichlorphon.

2.3 Bound

Pesticides could mineralize as bound compounds (Table 2). This mineralization increased with time. The bound compounds of trichlorphon, for example, were 0, 1.29%, and 25.66% of the applied radioactivity at the end of 1, 2 and 4 weeks of the experiment; and those of bensulfuron methyl were 8.61%, 16.28% and 18.75% respectively at the same interval. Highest percentage of bound compound were found for DDT and chlorpyrifos. At the end of 1, 2 and 4 weeks, the percentage of bound compound were 18.44%, 52.08%, 54.12% for chlorpyrifos and 38.30%, 43.99% and 42.54% for DDT respectively. At the end of 4 weeks of the experiment, the order of bound compound was: chlorpyrifos> DDT > BHC> fenvalerate> trichlorphon> mono crotophos> chlordimeform> bensulfuron methyl > chlorsulfuron.

The order of the ratio of bound pesticides to metabolized pesticides at the end of 4 weeks of the experiment was ranked as follows: chlorpyrifos 174.71, chlorsulfuron 74.19, bensulfuron methyl 48.08, DDT 46.24, BHC 36.81, mono crotophos 1.16, fenvalerate 1.01, chlordimeform 0.69 and trichlorphon 0.46.

2.4 Residues in aquatic ecosystem

Pesticides remained in aquatic ecosystem could be estimated by subtracting the radioactivities of volatile and $^{14}CO_2$ from total applied radioactivity. The residues of the pesticides, including parent pesticides and metabolites, at the end of 4 weeks of the experiment were in the order of: chlorsulfuron 99.79%, DDT 98.31%, bensulfuron methyl 97.73%, chlorpyrifos 91.93%, mono crotophos 81.14%, fenvalerate 72.86%, BHC 67.33%, chlordimeform 66.21% and trichlorphon 44.18%.

Chlorsulfuron is representative of sulphonylurea herbicides. Reports have appeared showing that this herbicide was chemically stable in alkaline environment and 'carry-over' from one year to the next can occasionally result in damage to succeeding sugar beet and other crops. Studies were carried out to study its persistence in prairie field soil; after 95

Tab. 2 Fate of pesticides in mini model ecosystem Bq

Pesticides	Total activity	Items	1 week Activity /%	2 week Activity /%	4 week Activity /%
DDT	2 139.3	Volatile	5.8(0.27)	8.4(0.39)	16.1(0.77)
		CO_2	1.2(0.05)	8.5(0.40)	19.7(0.92)
		Bound	819.3(38.30)	941.0(43.99)	910.0(42.54)
BHC	1 971.6	Volatile	370.6(18.80)	597.1(30.29)	626.5(31.78)
		CO_2	4.0(0.20)	17.1(0.87)	17.5(0.89)
		Bound	210.4(10.67)	556.8(28.24)	646.0(32.76)
Chlorpyrifos	3 166.0	Volatile	248.3(7.84)	275.3(8.69)	245.8(7.76)
		CO_2	6.8(0.21)	4.6(0.14)	9.9(0.31)
		Bound	583.7(18.44)	1 649.0(52.08)	1 714.8(54.16)
Trichlorphon	1 247.1	Volatile	8.7(0.69)	7.9(0.64)	3.5(0.28)
		CO_2	525.6(42.44)	550.7(44.16)	692.7(55.54)
		Bound	0(0)	16.1(1.29)	320.0(25.66)
Monocrotophos	3 008.8	Volatile	0.6(0.02)	2.2(0.07)	0.2(0.01)
		CO_2	325.9(10.83)	356.7(11.86)	567.2(18.85)
		Bound	5.6(0.02)	479.3(15.91)	660.1(21.94)
Chlordimeform	2 027.7	Volatile	10.0(0.49)	7.8(0.39)	43.3(2.13)
		CO_2	100.6(4.96)	282.8(13.95)	641.9(31.66)
		Bound	433.9(21.40)	322.9(15.92)	443.1(21.85)
Fenvalerate	589.6	Volatile	0(0)	0(0)	0(0)
		CO_2	93.4(15.84)	145.0(24.60)	160.0(27.14)
		Bound	106.6(18.09)	157.1(26.65)	161.9(27.45)
Chlorsulfuron	2 489.6	Volatile	0(0)	0(0)	0(0)
		CO_2	2.6(0.10)	4.5(0.18)	5.2(0.21)
		Bound	231.1(9.28)	287.8(11.56)	387.8(15.58)
Bensulfuron methyl	1 558.4	Volatile	7.0(0.45)	13.8(0.89)	29.3(1.88)
		CO_2	1.2(0.08)	2.5(0.16)	6.1(0.39)
		Bound	134.2(8.61)	253.6(16.28)	292.3(18.75)

weeks some 2 percent of the radioactivity was still in the form of chlorsulfuron[6]. It was also shown that 3% ~ 16% herbicide applied in May of one year was still detectable in the top 10 cm of soil a year later. By measuring the rate of degradation of chlorsulfuron in five soil of different pH values and at three depths, a half-life of longer than 600 days was recorded in some soil with pH values above 7.0[6]. Our results are consistent with these investigations, chlorsulfuron is also persistent in marine environment. Our previous studies also demonstrated that the herbicide was not bio-accumulative one (unpublished data). However, since the effective toxic concentration of chlorsulfuron to plant is very low, its effect on biota, especially on marine plants, should be further studied.

DDT is one of the most persistent and highest bio-accumulative pesticides. Our previous result showed that DDT could rapidly accumulate in fish, upon the exposure of the fish to ^{14}C-DDT for one day, about 94% of the DDT in water had already accumulated in fish[7]. Because of its intensive use in 1950's and 1960's in the world, the DDT residues are still detected, in spite of its use banned or restricted in most of the countries from the 1970s[8]. It has been recognized that its behavior in the tropical environment may differ significantly compared with temperate countries. Varca and Magallong[9] have demonstrated that the half life of DDT in tropical zone was about 6 months to 1 year, much shorter than in temperate zone, which was about 10 years. Our present results suggest that the half life of DDT in South China be longer than 1 year. Further studies are in progress for better understanding the fate of this pesticide in our subtropical zone.

Tejada et al[10] have studied the fate of some carbon-14 labeled pestcides in a model rice paddy ecosystem. Results showed that chlorpyrifos has strong affinity to the soil,

with an average of 91% absorption. ^{14}C-monocrotophos degrades rapidly in the soil. While it was not detectable at the 25 cm soil evel after 2 weeks, it took another 2 weeks to degrade to non-detectable levels at the 50 cm depth, and up to 73 days, at the 125~175 cm depths. Our present results for chlorpyrifos and monocrotophos was well consistent with the above report.

Trichlorphon is unstable and easy to be degraded by microorganisms in the environment. Its high production of $^{14}CO_2$ implies that the bound compound might not be the parent pesticide or its metabolites. Thus, its residues, including parent pesticide and metabolites, should be much less than 44.18% as shown above, because the $^{14}CO_2$ released from the pesticide might be assimilated by microorganisms in the ecosystem.

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研究标记农药归宿的微型模拟生态系统

钟创光* 陈舜华 Carvalho F P 赵小奎

摘　要　建立了 1种适合于研究标记农药归宿的微型模拟生态系统. 该系统集中在 1闪烁瓶内, 瓶中置 1玻璃试管, 管内装入 1 mL水和 0.5 mL沉积物以及标记农药. 试管上置聚氨酯棉花吸收挥发物, 生物代谢产生的 $^{14}CO_2$由闪烁瓶中的 NaOH吸收. 利用这一系统研究了 DDT, 六六六, 毒死蜱, 敌百虫, 久效磷, 杀灭菊酯, 杀虫脒, 绿磺隆和苄嘧磺隆等 9种 ^{14}C标记农药在微型海洋模拟生态系统中的归宿.

关键词　微型模拟生态系统, 标记农药, 归宿

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* 中山大学生命科学学院, 广州, 510275