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REGIONAL NETWORK ON PESTICIDES FOR ASIA AND THE PACIFIC

DP/RAS/88/031

THE REPUBLIC OF KOREA

Technical report: Findings and recommendations*

Prepared for the Government of the Republic of Korea
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of K. Nose,
consultant in pesticide specification

Backstopping officer: B. Sugavanam
Chemical Industries Branch

United Nations Industrial Development Organization
Vienna

* This document has not been edited.

V.92 50157

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EXPLANATORY NOTE

Local currency

UN rate : Won 712.000000

Abbreviation

ACPI : Agricultural Chemical Research Institute, Korea

RENAP : Regional Network on Pesticide for Asia

RDA : Rural Development Administration, Korea

MAFF : Ministry of Agriculture, Forest and Fishery, Japan

ETU : Ethylene ThioUrea

EBDC : Ethylene Bis(DithioCarbamate)

JMPR : Joint Meeting of Pesticide Residue

T-AID : Temporary Admissible Daily Intake

HL : Half Life

MRR : Maximum Residue Ratio

CRF : Controlled Release Formulation

ABSTRACT

Title : Pesticide Impurity, Soil Decomposition Test

Project No : DP/RAS/88/031/11-59

Objective : To give advice on " Identification Technics of Impurities in Pesticide Technicals " to a Regional Workshop ". To suggest necessary data for environmental safety.

Duration : One month, Oct.10 - Nov.8, 1991

The consultant adviced that setup specification should be launched from those pesticides patent of which already expired. He also suggested that MRR, which is derrived from HL as result of soil-vessel-test, will give a stable parameter as an estimate of environmental persistency.

I INTRODUCTION

The increased production and use of pesticide has brought awareness to safe development of pesticide production and use during the last 10 years. ACRI has been acted as a national coordinating organization in Korea for executing RENPAP project under UNIDO since 1982. A regional Workshop on Identification Techniques of Impurities in Pesticide Technicals were scheduled at ACRI around early October 1991. ACRI invited a consultant from Japan on the suggestion of Regional Coordinating Unit located at New Deli, India and the agreement of Regional Coordinating Unit. The consultant were requested to present a lecture on setup procedures and method of pesticide specifications during his stay in ACRI. Unfortunately, the Workshop was postponed in the future. Therefore the consultant's activities were done by discussion with his counterparts. Besides the impurity problem, the consultant proposed a basic idea to the soil decomposition test for the estimation of the environmental persistency.

II ACTIVITIES

A Impurity Problem

1. General Idea

Specification of pesticide should be announced in public. Recent development of pesticide industry supply us each pesticide by only one enterprise. The information of impurity existence both in quality and quantity belongs to rather secret of the enterprise. This character of impurity problem seems not to be compatible with industrial specification. In Japan as an enterprise wants to have a new pesticide registered to MAFF, it have to present necessary data for safety including the quality and quantity of hazardous impurity. These data were never announced in public. Under the condition that only one enterprise keeps the data about impurities, the specification will be made as the enterprise pleases. This kind of specification seems not to be useful. So, setup specification of impurity should be started from those pesticides patent of which already expired.

2. Pesticide under discussion

There must be no problems so long as impurities have little biological activity. A chemical is allowed to register as a pesticide under this principle. Unfortunately, the biological activity and danger of the impurities are recognized after the pesticide is used widely. Previous estimation of impurities in a new pesticide is not easy because of commercial reason. Now, two pesticide is in mind; ETU in EBDC and isomalathion and others in malathion.

ETU : The 1986 JMPR (FAO/WHO 1987) determined an estimation of AID for man of 0.002 mg/kg as a T-ADI. The limit to the ETU % in EBDC will be 0.5 %, following FAO specifications (FAO 1979). However, the method of chemical analysis should be based on HPLC because the high temperature of GC is liable to cause the transformation from EBDC to ETU. The analytical method can be easily set up from the method for residue analysis (Annex III). Analytical method of EBCD has better to be changed into the HPLC method as the carbon disulfide method is not selective. The method in Appendix III was applied to the residue analysis of tomato in Jakarta,1982.

Isomalathion, trimethyl phosphates in malathion: These impurities are believed to be responsible in the accident 1976 Pakistan. The limit % to the impurities in malathion is necessary to be investigated further.

Dioxine in pesticides derived from polychlorophenol: The standard substance 2,3,7,8-tetrachlorodibenzo-p-dioxine should be handled with the same caution as radio-isotope. The determination needs expensive GC-MS. The limit % to the Dioxine in pesticide is still obscure. Suspending setup specification is better until enough data accumulate.

Optical isomers in pyrethroid: It is liable to cause similar accumulation as ß-BHC. Suspending setup specification is better until enough data accumulate.

Question: If an unexpected accident occurred after a pesticide has been registered, what action will be taken by your government, Japan?

Answer: Enterprises have to renew their register each 3 years in my country, Japan. Usually unexpected hazards are liable to come up after the pesticide has been used widely. The government will continue to investigate the cause of accident until the time of renewal followed by no acceptance of the renewal.

B Soil Decomposition Test

1. General Idea

Besides the impurity data, MAFF requires the results from soil decomposition test. There are two categories of soil decomposition test. One is the field test and the other is the vessel test. The field test is hard to give reproducible results. The interpretation from the vessel test is more important and HL should be used as the parameter. Usually the vessel test gives a longer HL than the field test because the latter involves various factors like evaporation, run off, leaching, etc. besides of biological decomposition. In the vessel test, vessels are placed under 25-30 C. This may be higher than in the condition of the field test in Japan. This suggests that the other factors than biological decomposition are not negligible.

However, the precise estimation of the other factors is not easy. So HL from vessel test seems to be only stable parameter for soil persistency. Soils are inherent in countries. The test should be executed with the soil and under the temperature of each country.

2. Principle

2-1 Decomposition Pattern

When log(concentration) is plotted against time, there will be three types of curve drawn. The ideal one is straight. The cliff type the slope of which is small at early stage and then becomes steep later, is often observed when breaking microorganism accumulate. In this case, the HL calculated from the earlier data is longer than one from the later. The longer HL should be adopted as the parameter for environmental safety. The third type shows the pattern like hill foot. The HL from the later data is longer than one from the earlier. Later are data, larger the HL is. This double principle is overcome by the multi-site theory.(Annex IV).

2-2 Multi-site theory

For the ideal case, the equation will be written,

$C = C0 \exp(-kt)$ .....(1)   half life = $(\ln 2)/k$ .....(2)

where C is pesticide concentration in soil, t elapsed time, C0 and k are constants of initial concentration and decomposition rate, respectively.

For hill-foot type, the equation will be written,

$C = C1 \exp(-k1t) + C2 \exp(-k2t) + C3 \exp(-k3t)$ ....(3)

$HL1=\ln 2/k1,\ HL2=\ln 2/k2,\ HL3=\ln 2/k3$ ....(4)

$C0 = C1 + C2 + C3$ ....(5)

Of course it will be able to write nonlinear curves in another way. This is one choice. In equation (3), the number of term is usually 2, but sometimes 3 term equation gives good accordance between observed data and the curve. More than 3 terms gives us difficulties in the calculation. In the equation (3), 6 parameters as C1, C2, C3, k1, k2, k3 must be estimated. From estimated parameters, it is indicated that C1/C0 part of applied pesticide decomposes with HL1, C2/C0 with HL2, and C3/C0 with HL3.

2-3 MRR

MRR is defined as

$$\frac{\text{total residue by infinitive times of application in a same interval}}{\text{residue just after the single application}}$$

MRR has a fixed value. When pesticide is applied repeatedly in the interval of HL, MRR will never exceed 2. This is true even in the

equation (3). MRR for the hill-foot type is calculated as
C1/C0(1-exp(-k1t)) + C2/C0(1-exp(-k2t)) + C3/C0(1-exp(-k3t)) ....(6)
or

C1/C0(1-exp(-tln2/HL1))+C2/C0(1-exp(-tln2/HL2))+C3/C0(1-exp(-tln2/HL3)) ....(6'), where t is the interval and reasonably 365 days.

2-4 Estimation of Parameters

It is well known that the two parameter estimation is always possible by the least square method. Sometimes it does not converge in more than 2 parameter system. Among various methods for nonlinear least square, the SIMPLEX is excellent. This program is offered as a subroutine of FORTRAN program. The user must write main part and sentence function defined from his equation. A microcomputer equipped with the coprocessor is available for the calculation.

3. Example of bromacil under the tropical condition

Under the tropical condition, the water loss from test vessels gives us a serious problem caused by disturbance of microorganism . A stopper is designed for preventing water loss from test vessels. Finally, it is gained that 0.61 part of applied bromacil decomposed with 4.8 days of HL and 0.39 part with 189 days of HL (Annex IV).

Question: Some pesticides are effective in CRF. Pesticides in CRF might have long HL values to exceed the limit in spite of the short HL of pure substance. What principle should be applied from the standpoint of environmental safety.

Answer: The vessel test is applied for pure chemicals and the field test for formulations in Japan. As long as HL is short on the vessel test, formulations making HL longer will be allowed as exceptional cases as formulation material have no problem.

III RECOMMENDATIONS

A Recommendations to the group of ACRI

1. Investigation to setup specification should be started from those pesticides patent of which expired such as ETU in EBDC and isomalathion and others in malathion.
2. The vessel method for soil decomposition test provides a stable parameter MRR as an estimate of environmental persistency.
3. The IBM personal computer 55 should be equipped with the coprocessor for the higher mathematic calculation.

B Recommendation to UNIDO

A more intensive consultation on pesticide persistency in the environment has to be provided to organize a regional net work for the pesticide safety.

B. Sugavanam/rp
25 May 1990

UNIDO

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

JOB DESCRIPTION

DP/RAS/88/031/11-58

Post title	Consultant on pesticide specification
Duration	1.0 m/m
Date required	August 1990
Duty station	Suweon, Korea
Purpose of project	To promote regional co-operation in the safe development and management of pesticides in the Asia region.

Duties

1. To provide information and training of counterpart on
   a) general schemes on establishment of pesticide specification;
   b) required parameters for set-up of pesticide specification;
   c) relation between specification parameters and biological outputs;
   d) confirmation of specification, in particular impurities in technicals and formulated products.

2. To suggest efficient utilization of existing instruments to confirm specifications.

..../..

Qualifications

Scientist with considerable experience in the area of pesticide chemistry, biology as well as pesticide registration work.

Language

English

Background information

Asia region, during the last 20 years, has developed infrastructure and facilities for pesticide manufacture and formulation. The increase in consumption of fertilizers and pesticides is reflected in the great leap forward in agriculture production in many countries. This has resulted in many countries becoming self sufficient and a few countries becoming major exporters of food grains, fruits and cash crops.

The increased production and use of pesticides also brought with it awareness to the safe development of pesticide production and use. As an innovative approach, UNDP/UNIDO sponsored a project in 1982, to have a regional approach to address to the various problems associated with the production and use of pesticides. This project in its first phase provided training, consultancy services and organized seminars, workshops, covering number of aspects related to pesticides. These areas included:

- Harmonization, trade and tariff regulations;
- Quality control;
- Formulation technology;
- Toxicology;
- Regional harmonization in registration of pesticides;
- Regional pesticide data collection;
- Residue analysis.

Based on the benefits accrued , the project has been extended till 1992 and will put emphasis on formulation, effluent control, environmental toxicology, quality control and residue analysis. As a part of this programme, the formulation technology/course is being organized in New Delhi in collaboration with the Pesticide Development Programme India.

Annex II

Counterparts

NAME	POSITION	AFFILIATION
Dr. Young-Sun Park	Director General	ACRI,RDA
Dr. Young-Ku Kim	Director	Pesticide Chemistry Division
Dr. Jeang-Oon Lee	Director	Pesticide Biology Division
Dr. Young-Ho Cheong	Director	Pesticide Safty Division
Dr. Byung-Youl Oh	Chief	Pesticide Formulation Lab.
Dr. Yang-Ho Park	Cheif	Combined Pesticide Formulation Lab.
Dr. Ki-Suk Sung	Chief	Botanical Pesticide Lab.
Dr. Yong-Chul Choi	Senior Researcher	Pesticide Biology Division
Dr. Chung-Kil Kang	Researcher	Pesticide Biology Division
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Mr. Jin-Hwa Kim	Researcher	Pesticide Formulation Lab.
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Mr. Seung-Sun Park	Researcher	Combined Pesticide Formulation Lab.
Mr. Oh-Kyung Kweon	Researcher	Botanical Pesticide Lab.

Annex III

KAZUO NOSE
OCT., 1991

DITHIOCARBAMATE FUNGICIDE

I Dithiocarbamate

1 Reagent

1-1 Solvent: methanol, hexane, acetonitril, and chloroform

1-2 Chemicals: cysteine hydrochloride, methyl iodide, EDTA-tetraNa, tetrabutylammonium hydrogene sulfate (TBA), anhydrous sodium sulfate, and sodium hydroxide.

1-3 Glassfiber filter

2 Preparation

2-1 Extraction reagent: Dissolve 50g of cysteine hydrochloride and 50g of EDTA into 1 l of water and then adjust pH 9.5-10 with 10 N NaOH solution.

2-2 Ion pair reagent: Fourteen % TBA solution.

2-3 Methylation reagent: Dissolve 7.0g of methyl iodide into 100 ml of chloroform and mix it with 300 ml of hexane.

3 LC condition

3-1 Column: Zorbax ODS 4mm, 25 cm length.

3-2 Eluent: Acetonitril + water (1:1).

3-3 Flow rate: 1 ml/min.

3-4 Detector: UV 272 nm.

4. Procedure

Ten μg to 100 μg of dithiocarbamate is mixed with 100 ml of extraction reagent followed by shaking for 30 min. The solution is filtered with a sheet of glassfiber filter. Add 5 ml of ion pair reagent to the filtrate and then adjust pH 7.5-7.8 ml with 6N-HCl. Add 40 ml of methylation reagent to the solution followed by shaking for 5 min. After separating the organic layer, the aquatic layer is mixed with 20 ml of methylation reagent followed by shaking for 5 min. again. Collect organic layers and allow it to stand for 30 min. Dehydrate the organic solution and evaporate to dryness. The residue is dissolve into 2 ml of methanol and 20 μl of the methanol solution is injected to the LC.

By Nobuyuki Kibune etal. 1982 Nihon Shokuhinbunseki Centre

II Ethylenethiourea (ETU), residue analysis

1 Chemical name: 2-imodazolidinethione C3H6N2s mw:102.17

2 Reagent: Methanol, dichloromethane, hexane, pottasium fluoride, Extrelut 20 (Merk)

3 LC condition

3-1 Column:Senshu Pak ods-2201-N 6.0 mm, 20cm length

3-2 Guard column: RP-8 (Brownlee) 4.6mm, 30mm length

3-3 Eluent:Methanol+water (5+95, v/v)

3-4 Flow rate: 1 ml/min.

3-5 Detector: UV 240 nm

4 Calibration

Purified ETU is dissolved into the eluent and 0.1 - 3 ppm standard solution is prepared. 10 μl of the solution is injected to the LC.

5 Precedure

Twenty grams of vegetable homogenate is taken into a 300 ml Erlenmyer flask. After adding 10 g of potassium fluoride and 100 of methanol-water

(3+1,v/v), the whole mixture is shaked for 30 min. The mixture is filtered with suction. The residue is washed with 50 ml of methanol-water. The filtrate and washings are combined and concentrated to 20 ml under reduced pressure and 50 ℃. To the concentrate 100 ml of water is added followed by washing with 50 ml of hexane. The aqueous layer is concentrated to 10 ml.

The concentrate is adjusted pH 8 or more with 1 ml of 1 % ammonia solution and transfered into a Extrelute column. The Extrelute is allowed to stand for 20-30 min. and then eluted by 100 ml of dichloromethane. The eluate is evaporated to dryness under reduced pressure and less than 40 ℃. The residue is dissolved into methanol-water (5+95,v/v) and 10 μl of the solution is injected into the LC.

6 Detectable limit: 1 ng

By H. Kobayashi etal :J. Pesticide Sci., 11 81-84 (1986)

Annex IV

Note

A Multi-site Decay Model of Pesticide in Soil

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(Received April 14, 1986)

MODEL

The decay curve of a pesticide in soil is expected to be a straight line when its logarithmic concentration is plotted on the ordinate and time on the abscissa,

$$\ln(C/C_0) = -kt \quad \text{or} \quad C = C_0e^{-kt} \qquad (1)$$

where C is the concentration of the pesticide in soil, C_0 the estimated initial concentration, t the lapsed time after application, and k the decay rate constant. The equation is derived from the differential equation of the first order reaction.

$$dC/dt = -kC \qquad (2)$$

But the real decay curve is not always straight. Decay patterns often shape a foot of mountain. Hamaker explained various curves by the multi-order decay,[1] but few curves fit well to the high order decay.

When incorporated into soil, a pesticide is supposed to be distributed to several independent sites, where the decay rates differ. The decay is expected to be represented by the following equations,

$$C = \sum_n C_n \exp(-k_nt) \qquad (3)$$

$$C_0 = \sum_n C_n \qquad (4)$$

where C_n is the initially distributed concentration and k_n the decay rate constant in the nth site. If k is equal to $k_1 = k_2 = k_3 = \ldots = k_n$, Eq. (3) reduces to Eq. (1). In another case in which the transport of a chemical between sites is free,

$$dC/dt = -k_1t - k_2t - \cdots, \quad k = k_1 + k_2 \cdots$$

the equation also reduces to Eq. (1).

CALCULATION

Ohkawa *et al.*[2] reported different decay patterns of fenvalerate in different soils; a straight decay pattern in an Azuchi soil and a shape of foot of mountain in a Kodaira soil. The data are calculated by Eq. (3) utilizing a Acos-6 computer in the Norin Computer Center, Tsukuba, by the nonlinear least square method using SIMPLEX.[3,3)] The results are shown in Fig. 1. Ln C is plotted on the ordinate and t on the abscissa. The equation fits satisfactorily to the data. A numeral after 'Half Life' is calculated from Eq. (1) and numerals in the next line are from Eq. (3) and they are C_1, $\ln 2/k_1$, C_2, $\ln 2/k_2$, ..., respectively, with $\ln 2/k$ representing the half life.

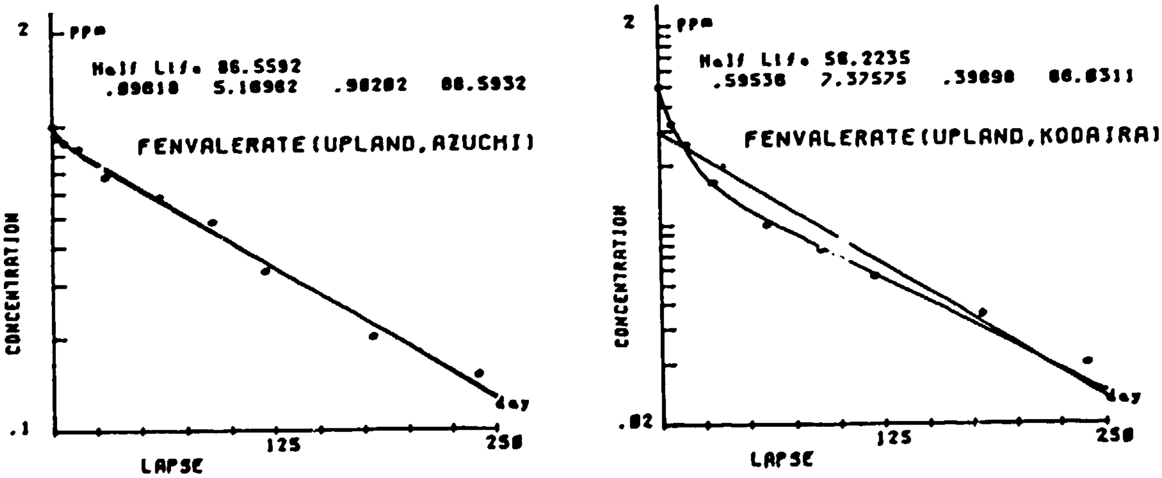

Fig. 1 Curve fitting of fenvalerate decay in soil.
The one-site model gives a straight line. The two-site model gives a curved line.

When C_0 is normalized to unity, the equation is;

$$C=0.60\exp(-0.0940t)+0.40\exp(-0.0105t)$$

for the Kodaira soil

$$C=0.10\exp(-0.134t)+0.90\exp(-0.00782t)$$

for the Azuchi soil

Six parameters were also estimated for Azuchi soil, but the AIC from the parameters, Akaike's Information Criterion (number of data) × ln (residual square sum) + 2 × (number of parameters), is larger than that from four parameters. Then the four parameter estimation is optimum for the Azuchi soil.

From the equation, fenvalerate in the Kodaira soil is estimated to decay at two different rates; 60% of the applied amount decay at 7.4 days of half life, 40% at 66 days. The Azuchi soil is also estimated to decay fenvalerate at two different rates; 90% at 89 days of half life and 10% at 5.2 days. In both cases one of the half lives is shorter and the other is longer than the half lives by the linear calculation.

COMPARISON WITH THE TWO-COMPARTMENT MODEL

Hill and Schaalje reported a two-compartment model.[6] Unfortunately the report has a serious misprint. In Eqs. (5)–(9) below, C_1 and C_2 are not constants but variables like in the Hill's report. The comparison between two models is shown in Fig. 2. The calculation should be as follows;

$$C=C_1+C_2 \tag{5}$$

$$dC_1/dt=-(k_s+k_r)C_1 \tag{6}$$

$$dC_2/dt=k_rC_1-k_dC_2 \tag{7}$$

$$\begin{aligned} dC/dt&=d(C_1+C_2)/dt=-(k_s+k_r)C_1+k_rC_1-k_dC_2\\ &=-k_sC_1-k_dC_2=-k_sC_1-k_d(C-C_1)\\ &=(k_d-k_s)C_1-k_dC \end{aligned} \tag{8}$$

From (6)

$$C_1=C_0e^{-(k_s+k_r)t} \tag{9}$$

From (8) and (9)

$$dC/dt=(k_d-k_s)C_0e^{-(k_s+k_r)t}-k_dC$$

$$dC/dt+k_dC=(k_d-k_s)C_0e^{-(k_s+k_r)t}$$

$$C=e^{-k_dt}\left(\int(k_d-k_s)C_0e^{-(k_s+k_r)t}e^{k_dt}dt+K\right)$$

$$=((k_s-k_d)C_0e^{-(k_s+k_r)t})/(k_s+k_r-k_d)+Ke^{-k_dt}$$

From the initial condition, $C=C_0$ at $t=0$

$$K=k_rC_0/(k_s+k_r-k_d)$$

Then

$$\begin{aligned} C&=C_0e^{-(k_s+k_r)t}+k_rC_0/(k_s+k_r-k_d)\\ &\quad\cdot(e^{-k_dt}-e^{-(k_s+k_r)t})\\ &=(C_0/(k_s+k_r-k_d))((k_s-k_d)\\ &\quad\cdot e^{-(k_s+k_r)t}+k_re^{-k_dt}) \end{aligned} \tag{10}$$

It is clear that parentheses are missed in the Hill's report. By comparing (3) with (10) after C_0 in normalized to unity,

$$\begin{aligned} &C_1'=C_1/C_0,\quad C_2'=C_2/C_0,\\ &C_1'=(k_s-k_d)/(k_s+k_r-k_d),\\ &C_2'=k_r/(k_s+k_r-k_d),\\ &k_1=k_s+k_r,\\ &k_2=k_d \end{aligned} \tag{11}$$

Then,

$$k_d=k_2,\quad k_r=C_2'(k_1-k_2),\quad k_s=C_1'k_1+C_2'k_2 \tag{12}$$

Thus, the parameters from the two-site model can be transformed to those from the two-com-

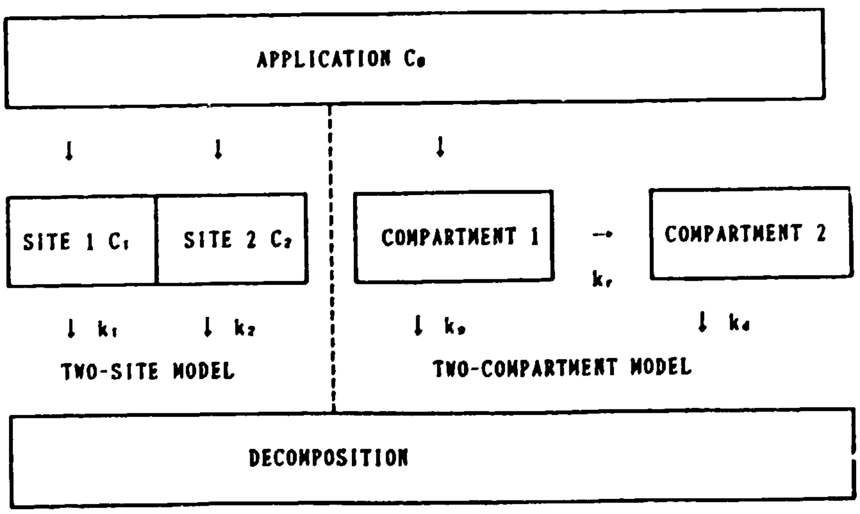

Fig. 2 Two decay-models.

partment model. The data on fenvalerate were applied to the Eq. (10) directly using SIMPLEX, but to estimate parameters which would give a minimum residual square sum was difficult. The mathematical complexity of equations seems to cause this difficulty. Two-compartment parameters calculated from two site ones are $k_s=0.0606$ and 0.01995, $k_r=0.0334$ and 0.11409, and $k_d=0.0105$ and 0.00782 for the Kodaira and Azuchi soils; the corresponding half lives are 13 and 35, 21 and 6, and 66 and 89 days, respectively.

MAXIMUM RESIDUES BY SUCCESSIVE APPLICATIONS

When a pesticide is successively applied at the same rate at regular intervals T to a soil in which a two site decay is proceeding, R_m, the concentration in the soil just after the mth application is represented by Eq. (13) as the distribution ratio between two sites is supposed to be constant.

$$R_m=C_1'(1+e^{-k_1T}+e^{-2k_1T}+\cdots+e^{-(m-1)k_1T})+C_2'(1+e^{-k_2T}+e^{-2k_2T}+\cdots+e^{-(m-1)k_2T})=\frac{C_1'(1-e^{-mk_1T})}{1-e^{-k_1T}}+\frac{C_2'(1-e^{-mk_2T})}{1-e^{-k_2T}} \quad (13)$$

On the extremity $m\to\infty$

$$R_\infty=C_1'/(1-e^{-k_1T})+C_2'/(1-e^{-k_2T}) \quad (14)$$

One of sufficient conditions as a guide that R_∞ does not exceed 2 is,

$$C_1'\leqq 1-e^{-k_1T} \text{ and } C_2'\leqq 1-e^{-k_2T} \quad (15)$$

The relationship between e^{-365k} and the half life is shown in Table 1. The critical half life, which does not raise the residue level higher than double the single application rate, depends on the C', and the guide can be found from the table. For example, a set of up to 210 days for 0.7 of C_1' and up to 709 days for 0.3 of C_2' is admissible as a set of half lives which does not raise the residue level higher than double the single rate. When a pair of half lives does not satisfy Eq. (15), the exact calculation with Eq. (14) is required, and one can infer how high residue level goes up by the successive applications with a set of half lives.

Table 1 Residue ratio after a year and half life.

Residue ratio[a]	Half life (days)	k_n[b]
.0001	27	.0252338
.001	37	.0189254
.01	55	.0126169
.02	65	.0107179
.03	72	9.60701E-03
.04	79	8.81884E-03
.05	84	8.20749E-03
.1	110	6.30845E-03
.15	133	5.19759E-03
.2	157	4.40942E-03
.25	183	3.79807E-03
.3	210	3.29856E-03
.35	241	2.87623E-03
.4	276	2.51039E-03
.45	317	2.18769E-03
.5	365	1.89903E-03
.55	423	1.63791E-03
.6	495	1.39952E-03
.65	587	1.18023E-03
.7	709	9.77192E-04
.75	879	7.8817E-04
.8	1134	6.11352E-04
.85	1557	4.45257E-04
.9	2401	2.88659E-04
.95	4932	1.4053E-04

a) Residue rate one year after application of a chemical.

b) k_n: decay rate constant.

CONCLUSION

A multi-site decay model is successfully applied to the decay of fenvalerate in soil. The reasons why each site is independent and why there is no transport of the chemical between sites, remain to be studied further. The two-compartment model has a difficulty in estimating parameters, but the parameters can be transformed from the parameters of the two-site model. The multi-site model will be a useful tool to predict persistency of a pesticide in soil.

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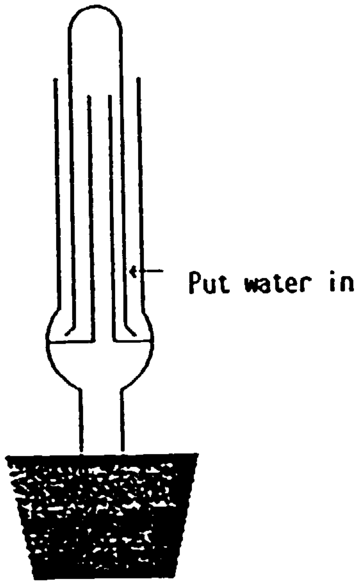
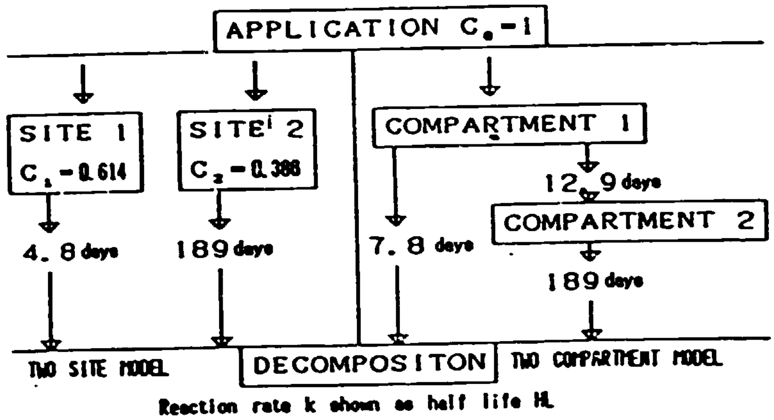
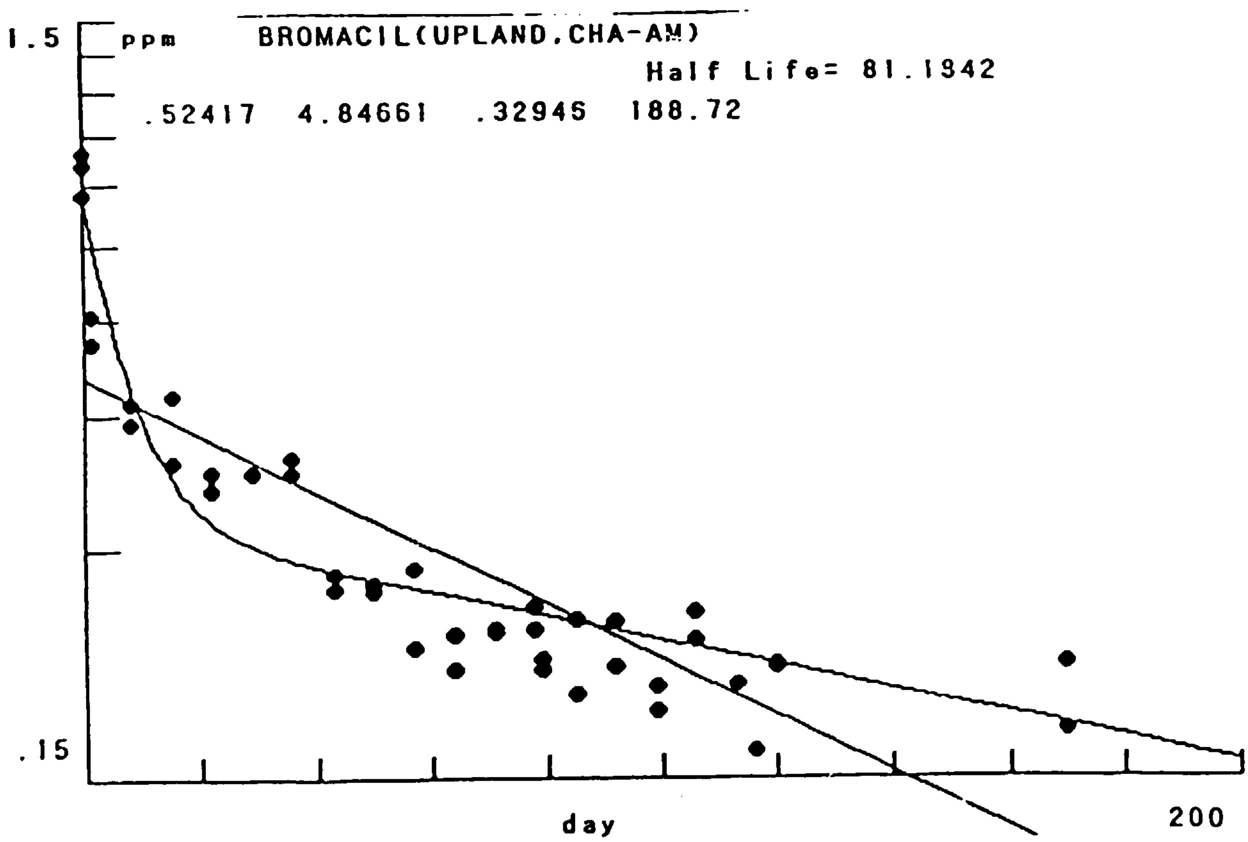
Annex V

Example : Bromacil decopmpsition under tropical conditions



Stopper
keeping moisture constant





Annex VI

UNIDO COMMENTS

The report deals with an important aspect related to impurities in technical materials. Most of the work carried out deals with the degradation of pesticides in the soil. The impurities in technical materials have caused great concern regarding their toxicology to mammals, biological activity in the field and unwanted side effects in the environment.

While the report mainly deals with the degradation in the soil, UNIDO would like to see more analytical work carried out both on the active ingredients and their formulations to give the advanced warning as to what to look for either as a metabolite or as impurities in the environment.

The report clearly looks into the future as more regulatory bodies will be asking the questions about the fate of active ingredients and their major impurities in the environment.

As the Republic of Korea is the Technical Co-ordinator Unit for Impurities in technical materials this report would be useful to RENPAP if they could make necessary arrangements to extend to various impurities likely to be present in pesticides commonly used in the RENPAP member countries.