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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 L. Vollner, consultant
in R & D controlled release pesticide formulations

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United Nations Industrial Development Organization
Vienna

* This document has not been edited.

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Abbreviations (as they appear in the report)

RENAP	- Regional Network on Pesticides for Asia and the Pacific
UNIDO	- United Nations Industrial Development Organization
ACRI	- Agricultural Chemicals Research Institute
ITTC	- International Technique Cooperation Center
RDA	- Rural Development Administration
FAO	- Food and Agricultural Organization of the United Nations
IAEA	- International Atomic Energy Agency
UNDP	- United Nations Development Programme
CSF	- Gesellschaft für Strahlen und Umweltforschung, Munich
CRF	- Controlled Release Formulation(s)
IBP	- Iprobenfos, (Kitazin P)
BPNC	- 2-sec-butylphenyl methylcarbamate, (Fenobucarb)
GR	- granules
WP	- wettable powder
EC	- emulsifiable concentrate
SL	- soluble concentrate

ABSTRACT

Title: Controlled Release Pesticide Formulation

Project No: DP/RAS/88/031/11-53

Objectives:

- To review activities of the Pesticide Formulations Unit at the Agricultural Chemicals Research Institute, Rural Development Administration, Suweon, Republic of Korea;
- to assist in selecting formulation types and materials, and
- to make further recommendations within the scope of CRF, in accordance with the needs of the country.

Duration of the mission: 1 month, September 1990

As the main conclusion of the mission, selection of pesticides and formulating agents for CRF could be managed. The selected pesticides are as follows: IEP, tricylazol, probenazol, isoprothiolane (fungicides), butachlor, metolachlor, pendimethalin, napropamid (herbicides), fenitrothion, diazinon, BPNC and cartap (insecticides). As formulating agents natural polymers were recommended, rather than thermoplastics. Such natural polymers include polysaccharides, like alginates and cellulose derivatives, like hydroxy-ethyl-cellulose.

Combination of pesticides and fertilizers in CRF was regarded as a good opportunity to improve application technique and to save costs of application. Urea, as the main fertilizer for paddy-rice, has been selected.

I . INTRODUCTION

A. General remarks

One of the major deficiencies in current pesticide technology is that pest control may be very temporary even with the best pesticide available. Pesticides may often be applied in excessive amounts to maintain the necessary levels of activity during the time period for which pest control is most urgently needed.

Losses to the environment and from environmental actions prevent most of the pesticide from reaching its biochemical site(s) of action in target species.

New formulation technology can be higher effective in increasing pesticidal effectiveness. A few of the parameters of pesticide efficiency that can be improved with better formulations include volatility, photodecomposition, and poor penetration into target species. This field is in its infancy, and research on formulation needs to be greatly expanded, especially in controlled release technology.

Within the RENPAP project, the Pesticide Formulation Group of ACRI, RDA, decided to make more efforts moving into this modern direction of pesticide formulations and requested a one-month consultation from UNDP and UNIDO.

B. Controlled release concept

CRF of pesticides are defined as depot systems which continuously release their toxic constituents into the environment over a specified period of time, usually months to years (1). According to this definition, such formulations can be successfully employed where a chronic exposure to biologically active compounds is required over a longer period.

Initial work was concerned with the production of protective coatings for sonar systems in marine ecosystems. By means of antifouling paints or rubber coatings containing tri-n-butyl-tin oxide, the growth of marine organisms on sonar domes, buoys and hulls in the water could be effectively prevented (2,3).

C. Systems for CRF

Controlled release systems are divided into two main groups such as the group of physically incorporations and such as the chemically linked ones, which again are further subdivided (4).

Physical systems

Migration control by membranes:

- microencapsulation
- macroencapsulation
- other membranes

Migration control without membranes:

- capillary systems (hollow fibres)
- porous polymeric substrates and foams
- polymeric gels
- osmotic pumps

Laminate systems

Monolithic systems: solutions and dispersion in non-porous polymers

- Migration without matrix erosion
- Migration caused by matrix erosion

Chemical systems

Ionic linked pesticides

Covalently bound pesticides

- copolymers with pesticidal comonomers
- polymer analogous reactions of pesticides with polymers.

D. Advantages and disadvantages of CRF

Based on the structure principle, CRF have a number of advantages:

- reduction of the mammalian toxicity of the formulations;
- reduction of phytotoxicity;
- reduction of active constituent losses through evaporation and seepage
- reduction of active substrates degradation (in the matrix);
- reduction of an environmental contamination with pesticides, and
- prolongation of the period of activity.

Compared to the advantages, there are also several fundamental disadvantages connected with these formulations, which make it necessary to carry out a risk/benefit analysis in each individual case before expensive new developments are initiated from the multiplicity of formulation possibilities. The following points represent, to date, a large

unknown quantity:

- behaviour of the polymer matrix in the environment:
- behaviour of polymer additives such as plasticizers, stabilizers, antioxidants, etc., in the environment, as well as
- the long-term behaviour of the degradation products of the matrix and the additives at the application site, and their transfer into other environmental media.

II. ACTIVITIES

A. Review of previous activities of the group

1. Pesticide formulations in general

The working group started its activities 1981 and made considerable contribution 1981 to the field of pesticide formulations. It developed e. g. a micro - granule formulation (5) against the rice plant insect, brown plant hopper (*Nilaparvata lugens*), which allows to increase the deposition of pesticides on the rice shoots and decreases drift to other areas.

Furthermore, the group developed a very effective fumigant formulation for greenhouse applications, which considerably reducing contamination of plants and soil.

2. Controlled release formulations

Within a FAO/IAEA project (R0K/5/025), the group carried out 1985/86 some CRF, using radiolabelled pesticides for evaluating properties of formulations.

These activities included pesticides like tricyclazol and IBP for improving efficacy of formulations in the control area of leaf and neck blast (*Pyricularia oryzae*) of rice plants (*Oriza sativa* L., chucheongbyeo). Some natural polymers, like starch and kraft lignin were used as formulating agents. The group also tested a hydroxy-ethyl-cellulose (Natrosol) - carbofuran formulation, which was developed by the expert (6), and supplied 1986 by IAEA.

Since the group joined late to the terminatig project ((see IAEA Final Report, (7)) no significant progress could be reached during the short period.

B. Selection of problem areas and of pesticides

1. Paddy rice

It could be agreed after intensive discussions that the main target for pesticide applications, thus for application of CRF is the rice paddy (Annex II), with its attacking pests. The most serious problem is on one hand the fungi, rice blast, which occurs in two forms, namely the leave blast and the neck blast, and on the other hand the insect brown plant hopper. During this period, fungicides are applied 3 to 4 times. To reduce application frequency CRF could help to support fighting against fungi deseases. Fungicides selected in order of priority are:

tricyclazol, 12 (Annex N): IBP, 6: probenazol, 11:
and isoprothiolane, .7.

The brown plant hopper appears from July to September. The application of insecticides during this period is not very successful for two reasons. Firstly, the widely used systemic insecticide carbofuran will not be taken up by plants in necessary toxic quantities because of the slow biological activity of the plants. And secondly, sprays hardly reach the lower part of the stems, where insects sitting. Thus, high quantities of pesticides has to be used to eliminate the insects, short before ripeness of grain. CRF could significantly help to solve these problems.

The less toxic (than carbofuran) carbamate insecticide, BPNC, 1, the bis-thiocarbamate, cartap, 3, and furthermore the most widely used herbicide butachlor 2 have been selected for this area.

2. Vegetables, fruit-trees

Generally occurring insects like moths, mites etc. on vegetables and fruit trees are widely treated with the insecticides diazinon, 4 and fenitrothion, 5, which are selected for CRF, as well.

To improve herbicides efficacy for upland applications, following herbicides have been selected (in order of importance): pendimethalin, 10:
napropamid, 9 and metolachlor, 8.

C. Selection of formulating agents

First priority for selecting formulation materials was to review possible natural sources, like agricultural wastes in Republic of Korea. Since those materials are few and mostly used for animal feed or as a soil nutrient, further searching was necessary. It was agreed, that artificial polymers are less practicable in the selected problem areas. Thus, natural polymers should remain the choice of quality.

III. RECOMMENDATIONS

A. Recommendations to the group of ACRI

According to his experience (6,8), expert recommended to use polysaccharides (e. g. alginates) for less water soluble pesticide formulations, and to use cellulose or modified cellulose (e. g. hydroxy-ethyl-cellulose) for more water soluble type of pesticides.

According to the purchase of such materials, a most economic approach should be considered. (Wastes, e. g. shells of coconut from Philippines or latex from tropical countries could be considered).

According to the physical-chemical properties of the pesticides selected for CRF (Annex IV), following recommendations were made.

Pesticide	Action and Area of Appl.	Formulating Agent	Type of Formulation
1) BPNC	non-systemic I, rice	A + Ca, possible combination with carriers	CR CR - CR
2) Butachlor	systemic H, rice	A + Ca	
3) Cartap	non-systemic I, rice	N - cross linked	GR - CR
4) Diazinon	non-systemic I upland	A + Ca	SL - CR
5) Fenitrothion	contact I, vegetables	A + Ca	SL - CR
6) IBP	systemic I, rice	A + Ca	GR - CR
7) Isoprothiolane	systemic F	A + Ca	GR - CR
8) Metalochlor	upland H, vegetable	N - cross linked	GR - CR
9) Napropamid	upland H, fruit trees	A + Ca	GR - CR
10) Pendimethalin	pre-emergence H, upland	A + Ca	GR - CR
11) Probenazol	F, rice	A + Ca	GR - CR
12) Tricyclazol	F, rice	N - cross linked	GR - CR

I = insecticide, F = fungicide, H = herbicide, A = sodium alginate, Ca = Ca ions e.g. from CaCl₂, N = natrosol (hydroxyethyl-cellulose)

B. Recommendation to UNIDO

Further support for this important area of work needs technical and additional training inputs.

IV . CONCLUSION

Exper' discussed problems of pest control in the Republic of Korea and selected pesticides and formulating agents for CRF, together with the staff of ACRI.

He carried out some alginate formulations for laboratory and greenhouse testing.

He furthermore assisted in separation of impurities of the technical grade herbicide butachlor, and held two seminars, entitled:

- 1) Controlled Release Pesticide Formulations with Natural and Artificial Polymers, 14 September, 1990, and
- 2) Pesticides of the Future, 21 September, 1990.

After clearance with the management of his reserch center in Munich, expert will offer a training facility for Mr. Jin-Hwa Kim in March/April 1991 at the CSF - Institute of Ecological Chemistry.

V . LITERATUR

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- (3) Rubber World, 157:77, D.R.Wuerzer et al., 1967
- (4) Fundamental concepts of CR, CRC, Boca Raton,, A.F.Kydonieus, 1980
- (5) Development of pesticide formulations, ACRI Tech Bulletin, No.3, 1988
- (6) Distribution and metabolisms of carbofuran in paddy rice from CRF, L. Vollner et al., IAEA-SM-297/28, 1987
- (7) IAEA-Final Report, ROK/5/025, R. M. Wilkins, 24/3/1989
- (8) Controlled release insecticide formulations for tropical applications, L. Vollner, A. Chods-Esphanani, IAEA-SM-297/27, 1987
- (9) Agrochemical Year Book, 1990, Agricultural Chemicals Industrial Association, Republic of Korea



UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

JOB DESCRIPTION

DP/RAS/88/031/11-59

Post title	Consultant on R&D for controlled release pesticide formulation
Duration	1.0 m/m
Date required	October 1990
Duty station	Suweon, Rep. of Korea
Purpose of project	To provide regional co-operation in the safe development of management of pesticides in the Asia region.
Duties	<ol style="list-style-type: none">1. Recent approaches on controlled release formulation of pesticides2. Formulation techniques using biodegradable natural polymers3. Pesticide formulation techniques using thermoplastic polymers4. Quality control measures and evaluation schemes of controlled release formulation quality

Applications and communications regarding this Job Description should be sent to:

Project Personnel Recruitment Section, Industrial Operations Division
UNIDO, VIENNA INTERNATIONAL CENTRE, P.O. Box 300, Vienna, Austria

Qualifications Formulation chemist with experience in the area of pesticide chemistry, physics and polymer science

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:

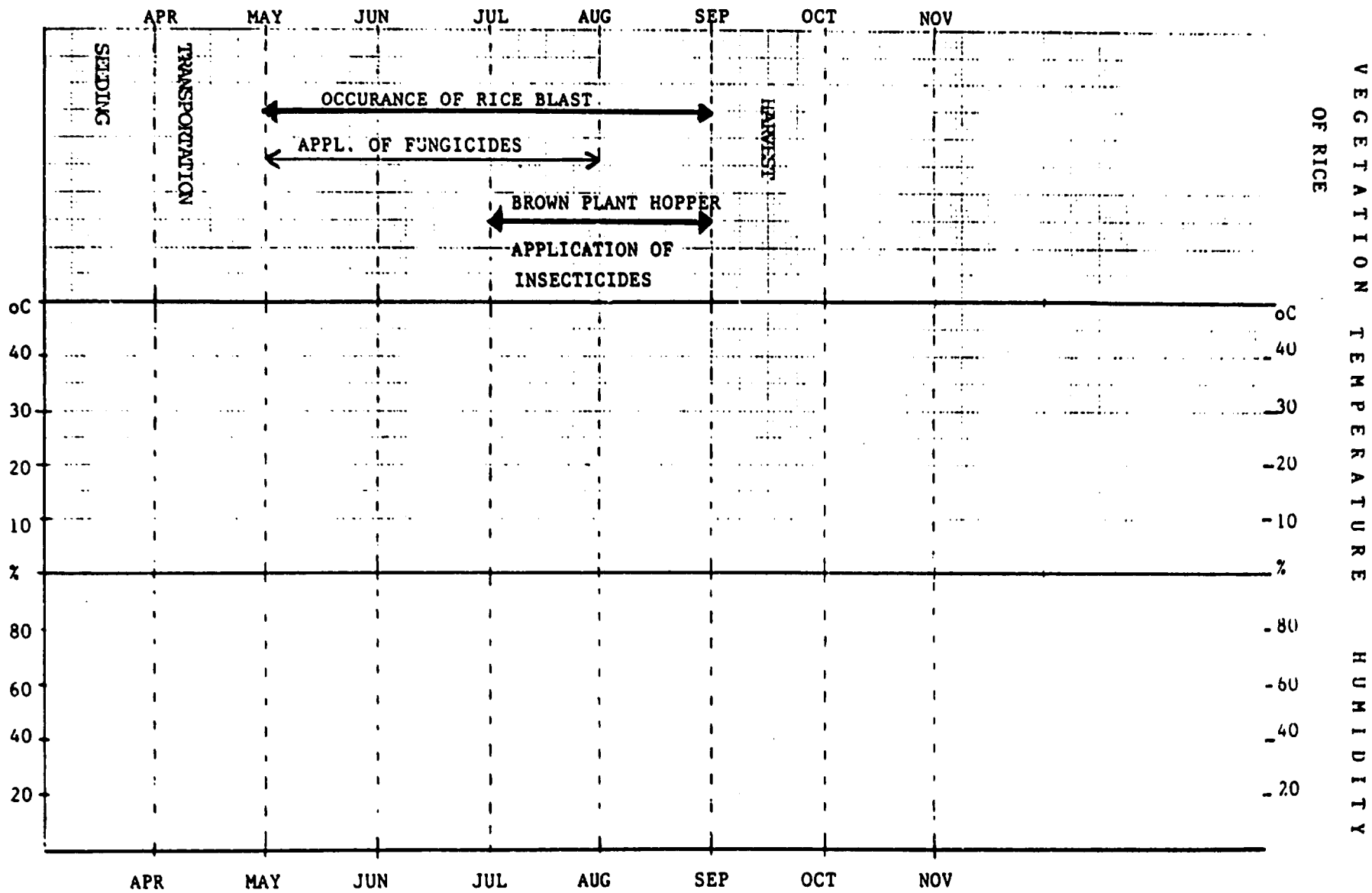
- Harmonization, trade and tariff regulations;
- Quality control;
- Formulation technology;
- Toxicology;
- Regional harmonization in registration of pesticides;
- Regional pesticide data collection;
- Residue analysis.

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

Persons contacted

Name	Position	Affiliation	Address
Dr. Young-Sun Park	DC	ACRI, RDA	249 Seodundong Kweonsunku Suwoen 441-100
Dr. Chae-Yun Cho	DC	ITCC, RDA	
Dr. Young-Ho Jeong	Director	Pest.Chem.Div.	
Dr. Byung-Youl Oh	Head	Formulation Lab	
Dr. Jin-Hwa Kim	In charge CRF	Formulation Lab	
Dr. Byung-Hun Song	Head	Chemistry Lab	
Dr. Oh-Kyung Keon	Jun. Researcher	Chemistry Lab	
Dr. Pyung-Cheol Park	Reg. Rep.	UNDP/UNIDO	Seoul
Dr. S. P. Dhua	Reg. Coordi.	UNDP/RENAP	New Delhi, India



ANNEX IV

Pesticides selected for CRF

Name of Pesticide	m. p/b. p o C	Solubility in 1 l Water	Annual Usage in Tonnes
1) BPNC	31 - 32 112 - 113	660 mg	EC 7,733 dust 1,735
2) Butachlor	-5 156	23 mg	GR 20,362 EC 277
3) Cartap	179 - 181 ---	200 g	GR 8,358 solu. 6,214
4) Diazinon	--- 83 - 84	40 mg	GR 4,099 EC 1,575
5) Fenitrothion	--- 140 - 150	14 mg	EC 1,173 WP ?
6) IBP	--- 126	1 g	GR 4,978 EC 3,229
7) Isoprothiolane	50 - 54 167 - 169	48 mg	GR 1,940 EC 1,857
8) Metalochlor	--- 100	530 mg	EC 34
9) Napropamid	75	73 mg	WP 525 EC 53
10) Pendimethalin	45 - 58	0.3 mg	EC 1,260
11) Probenazoi	--- 183 - 184	150 mg	GR 3,914
12) Tricylcazol	--- 187 - 188	1.6 g	WP 6,118 susp. 790