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SEED PELLETING AS AN APPROACH TO

HERBICIDE SELECTIVITY IN DIRECTSEEDED RICE

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF HAWAII IN PARTIAL FULFILIMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN AGRONOMY AND SOIL SCIENCE

AUGUST 1972

By

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SEED PELLETING AS AN APPROACH TO HERBICIDE SELECTIVITY IN DIRECTSEEDED RICE

By Dimyati Nangju

A dissertation submitted to the Graduate Division of the University of Hawaii in partial fulfillment of the requirements for the degree of Doctor of Philosophy

ABSTRACT

Field and greenhouse experiments were conducted at the Hawaii Agriculture Experiment Station on Kauai from June 1970 to May 1972 to study the feasibility of overcoming phytotoxicity of preemergence herbicides to directseeded rice (Oryza sativa L., var. IR8) by pelleting rice seed with an adsorbent. The effectiveness of adsorbent-pelleted seed was tested against three main herbicides: 3-amino-2,5-dichlorobenzoic acid (amiben), 2-chloro-2',6'-diethyl-N(butoxymethyl) acetanilide (CP 53619 or butachlor), and 2-tertiary butyl-4-2'-4'-dichloro-5' isopropyloxyphenyl-l,3,4-oxadiazoline-5-one (RP 17623). The properties of these herbicides with regard to adsorption, leaching, site of uptake, sensitivity and inherent susceptibility of rice to the herbicides, and herbicide diffusion to coated and uncoated seed were also studied to determine some basis for obtaining herbicide selectivity using adsorbentpelleted seed.

The phytotoxicity of the herbicides to directseeded rice was greatly reduced by pelleting pregerminated rice seed with activated carbon Darco G-60 three times using 50% polyvinyl acetate as an adhesive. The performance of the carbon-pelleted seed was influenced by both management and herbicidal factors. The most important management factors were

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method and rate of sowing, time of flooding, time and rate of herbicide application, herbicide formulations, coating quality, and temperature during seedling establishment. The most effective sowing method was broadcasting the pe11eted seed on nonf1ooded, puddled soil. Seed pe11eting did not protect rice when it was sown in water or below the soil surface under upland conditions, due to lack of intimate contact between herbicide and adsorbent and/or to the presence of standing water which inhibited seedling growth.

Evidence was presented to show that herbicide properties also influenced the effectiveness of pe11eted seed. In general, activated carbon pe11eting could not protect directseeded rice from herbicides which are lethal to transplanted rice, since the survival of pe11eted seed depended a great deal on the plant's ability to resist herbicide toxicity with increasing age. Activated carbon pe11eting protected directseeded rice from those herbicides which are lethal to germinating uncoated rice seed but not lethal to transplanted rice. The degree of protection, however, was dependent on herbicide adsorption on activated carbon and soil, the sensitivity of emerging seedlings to the herbicides, the rate of herbicide diffusion to rice seed, and the site of uptake of the herbicide. The adsorption efficiency of carbon coatings was influenced by the rate of herbicide diffusion and coating weight.

Seed pe11eting as an approach to herbicide selectivity in directseeded rice was most effective with CP 53619, but moderately effective with amiben and RP 17623. In this study RP 17623 was applied at the rate of 3.3 kg/ha or higher.

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When 3 percent methiocarb (4-methylthio-3,5-xylyl N-methyl carbamate)--an experimental bird repellent--was incorporated in the carbon pellet, the coating could protect rice seed from birds as well. The toxicity of the insecticide to rice seed was also reduced by activated carbon.

CP 53619 and RP 17623 were selective to upland rice up to 4.48 kg/ha when uncoated rice seeds were planted at least 3 em deep. Amiben and (2,4-dichlorophenoxy) acetic acid isopropyl ester (2,4-D IPE) severely injured upland rice since they were easily leached in soil and very toxic to emerging seedlings.

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CHAPTER 1. INTRODUCTION

Rice (Oryza sativa L.) is classified as a tropical and subtropical crop belonging to the family Gramineae. It is cultivated as far north as 49° and as far south as 35° , and from sea level to altitudes of 3000 meters (Pathak, 1968). Rice occupies almost one fifth of the total world area under cereals, and over half of the world's population eat rice as their staple diet.

There are two major ways of growing rice (Grist, 1962). In tropical Asia, rice is normally transplanted in well puddled soils. In the United States, Australia, Italy, Greece, Portugal, Morocco and Turkey rice is generally established by direct sowing either on upland soil, mud or in water. The directseeded method offers several advantages over the transplanted method in terms of time and labor costs (Mabbayad and Obordo, 1971). However, one of the biggest drawbacks of directseeded rice which often limits the grain yield is the weed problem (R. I. C. E., 1967).

Weed competition is generally greater for directseeded rice than for transplanted rice since weed seeds germinate at about the same time as rice. Handweeding or mechanical cultivation is nearly impossible because the grassy weeds are difficult to distinguish from rice seedlings; also, rice seeds are normally broadcast by hand or by airplane on mud or in water. Grasses are known to be the most serious kind of weeds as compared to broadleaves and sedges (International Rice Research Institute, 1969; Smith, 1969; Arai, 1967). Weed control with herbicides probably offers the best alternative for controlling weeds in directseeded rice. However, until recently research in this

direction has been limited. Very few of the presently available herbicides are nonphytotoxic to directseeded rice. The crux of the problem for herbicide selectivity is the similarity in the age, morphological, and also physiological characteristics of grassy weeds and rice plants.

Susceptible crops can be protected from toxic herbicides by directing herbicide application to weeds but not to the crop. But when the crop and the weeds grow very closely to each other, this technique is obviously impractical. However, several workers (Linscott and Hagin, 1967; Locascio, 1967; Brenchley, 1968; Kratky and Warren, 1970; Robinson, 1965; Hughes, 1964) have overcome this problem to a certain extent by applying activated carbon above or around the crop seed or root. The carbon adsorbed the toxic chemicals before they reached the seed or root, thus allowing it to grow unharmed. Their techniques, however, suffer from two drawbacks: (a) The weeds or weed seeds growing near or at the site where the carbon was applied were also protected, and (b) The techniques are either inefficient, complicated or expensive. A more reliable, better and simpler technique certainly has to be developed to correct these deficiencies. Pelleting seed with activated carbon or other adsorbents may be the answer to this problem. This method has been used successfully in microbiology (Norris, 1967), pathology (Brockwell, 1963) and other studies, but has not been fully investigated for use in weed science. In weed science, the primary objective of the use of adsorbent-pelleted crop seed is not only to get adequate protection from toxic chemicals but also to obtain weed control.

The objectives of this study were therefore as follows:

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a. To evaluate the feasibility of adsorbent-pelleted rice seed as an alternative technique in achieving herbicide selectivity in directseeded rice.

b. To find the best combination of pelleting materials from among several adhesives and adsorbents.

c. To evaluate, using the best pelleting materials obtained in (b), the influences of water management, method and rate of seeding, soil type, and mode, formulation, method, rate and time of herbicide application on the effectiveness of adsorbent-pelleted rice seed.

d. To determine the basis of herbicide selectivity for adsorbentpelleted rice seed on herbicide properties such as adsorption, leaching, site of uptake herbicide diffusion and inherent susceptibility of rice crop to herbicides.

CHAPTER II. REVIEW OF LITERATURE

Present Status of Chemical Weed Control in Directseeded Rice

Weed control is basic to agricultural development especially in wet tropical regions which have very serious weed problems (Furtick, 1967). The importance of weeds in rice and other crops is well documented (Klingman, 1961; Anon., 1968; Arai, 1967; Smith, 1967 and 1970; Matsunaka, 1970). Briefly, weeds reduce yield through direct competition for nutrients, C02, light, space and water. Grain yield can be reduced as much as 60 percent (Vega and Punzalan, 1968). Weeds serve as alternate hosts of insect pests and diseases, reduce the quality of harvested products, plug irrigation and drainage canals, and increase costs of production, harvesting, drying and cleaning.

Weeds can be partially controlled by cultural practices such as thorough land preparation, proper water and fertilizer management, use of weed-free seed, crop rotation, and land levelling (Nester, 1964). However, chemical methods by using herbicides in combination with cultural practices were more effective for weed control than either method alone (Smith, 1965).

Chemical weed control in rice began with the use of (2,4-dichlorophenoxy)acetic acid $(2, 4-D)$ in the late $1940's$. By 1950 2,4-D and ((4-chloro-o-tolyl)oxy)acetic acid (MCPA) were widely used in both transplanted and directseeded rice in temperate countries to control aquatic, broadleaf and sedge weeds (Shigezane, 1967; Smith, 1967). Later other herbicides such as (2,4,5-trichlorophenoxy)acetic acid $(2,4,5-T);$ 2- $(2,4,5-T)$; 2- $(2,4,5-T)$ acid (silvex); $2-((4{\text{-chloro-o-toly1}})$ oxy) propionic acid (mecoprop); $4-((4{\text{-chloro-o-toly1}})$ oxy)butyric acid (MCPB) and 4-(2,4-dichlorophenoxy)butyric acid

(2,4-DB) were also proven to be able to control these weeds (Smith, 1970). All these herbicides are normally applied about 45 days after sowing. Earlier or later application than this will cause severe injury to rice plants (Smith, 1967).

Grassy weeds, however, still remain ^a big problem. Barnyard grass (Echinochloa crusgalli (L.), Beauv.) is one of the most troublesome weeds in nearly all areas of the world that grow rice (Oelke and Morse, 1968; Holm, 1969). Nine grass plants per square meter in a rice stand of three plants per square meter reduced rice yield 57 percent (Smith, 1967).

In 1960, isopropyl m-chlorocarbanilate (CIPC) was introduced to rice farmers for the control of grassy weeds. It gave satisfactory grass control at the rate of 6 to 8 lb/A (6.7 to 8.9 kg/ha) applied 3 days after rice emergence. Its selectivity is based on the fact that Echinochloa seedlings produce their first node near the soil surface, whereas rice seedlings develop the first node well below the soil surface (Baker, 1960). However, critical requirements for effective grass control without crop injury restricted its use to a small acreage.

In 1961, the Agricultural Extension Service of the United States Department of Agriculture recommended the use of 3',4'-dichloropropionanilide (propanil) in controlling grasses and certain broadleaves. Brandes (1963), Kampmeier (1963), Plucknett and Younge (1964), Steel (1966), Fischer, et al. (1966) reported that propanil at 3 to 5 lb/A (3.3 to 5.6 kg/ha) was effective for control of barnyard grass when it was at ² to ³ leaf stage. Propanil is selective because rice can detoxify it to 3',4'-dichloroactanilide, thence to 3',4'-dichloroaniline

and lactic acids, while barnyard grass accumulates $3', 4'$ -dichlorolactanilide to lethal proportions (Yih, et al., 1968).

Although propanil was once widely used in the United States, Australia, Europe and South America, it is now being gradually replaced by S-ethylhexahydro-lH-azepine-l-carbothioate (molinate), a new and more effective grasskiller. Mueller and Oelke (1965), Mueller and Morse (1968), Oelke and Morse (1968), Smith (1968, 1970), and Moomaw and Kim (1968) reported that molinate, at 2 to 4 lb/acre (2.2 to 4.5 kg/ha) applied before flooding and prior to seeding rice into water or applied after rice emergence and after flooding dry seeded rice, controlled barnyard grass and other weeds with little or no injury to rice. The selectivity of molinate is based on much higher absorption and translocation of the chemical in barnyardgrass than in rice (Chem, et al., 1968).

Molinate is better than propanil in the following respects:

a. Molinate is systemic while propanil is a contact herbicide.

b. Being a contact herbicide, the performance of propanil is dependent on climatic factors. Propanil performed poorly in rainy climates (Nester, 1964; Guedez, et al., 1963; Moomaw, et al., 1966). Propanil also performed very poorly in the cool spring when the temperatures were below 10 C for a few days just before treatment (Smith, 1965; Watson, 1971). On the other hand propanil injured rice severely when daily maximum temperatures were above 35 C for several days before spraying (Smith, 1965).

c. Molinate produces a residual control of weeds for several weeks after application whereas propanil has none (Smith, 1968).

The International Rice Research Institute (IRRI) in the Philippines has been active in conducting weed control research on both directseeded flooded and unflooded rice. With regard to directseeded flooded rice IRRI (1968) found that 2-chloro-N-isopropyl acetanilide (propachlor) at 5 kg/ha and 4-(methyl sulfonyl)-2,6-dinitro-N,N-dipropylaniline (nitralin) at 2 kg/ha were moderately toxic to rice plants, but gave comparable grain yields to handweeded control due to high tillering capacity of variety IR8 which helped make up for the loss of tillers due to chemical injury. Other herbicides such as 2,3,5-trichloro-4-pyridinol (pyrichlor) at 0.2 kg/ha, 3-(p-chlorophenyl)-1,1-dimethylurea (monuron) at 1 kg/ha, 2,6-dichlorobenzonitrile (dichlobenil) at 2 kg/ha, and D,S-dimethyl tetrachlorothioterephthalate (glenbar) at 3.5 kg/ha were highly toxic to directseeded flooded rice.

In 1969 IRRI tried two methods of obtaining herbicide selectivity in directseeded flooded rice: (a) the application of preemergence herbicides several days before seeding to allow time for them to affect germinating weeds and to dissipate to levels sublethal to rice, and (b) the application of preemergence herbicides just before sowing rice seed coated with activated charcoal. These two methods were unfortunately not very successful. In the first method rice seed was broadcast too soon (3 days) after the application of herbicides, and subsequently were killed by the applied herbicides. In the second method the charcoal dispersed easily in the water-saturated paddy soil since no adhesive was used. In these experiments, the following herbicides were found to be toxic to directseeded rice: $M & B-13992$; VCS-438; C-5024; OCS-2l693 (all are coded compounds); methyl-N- (3,4-dichlorophenyl) carbamate (swep); 3,5-dibromo-4-hydroxybenzonitrile

(bromoxynil); 3,5-diiodo-4-hyroxybenzonitirile (ioxynil); 2,4,6-trichlorophenyl-4-nitrophenyl ether (CNP); nitralin; dichlobenil and pyrichlor.

However, recently IRRI (1971) found a safe chemical for use in directseeded flooded rice. The compound is S-(4-chlorobenzyl-N, N- diethylthiol carbamate (benthiocarb). Applied at 6 days after sowing (i.e. 2 to 3 leaf stage of grassy weeds) at the rate of 1 kg per ha it controlled all the annual weeds completely without causing any injury to rice plants. Obien, et al. (1971) obtained similar results with benthiocarb in Hawaii. They also showed that 2-tertiary butyl-4-2',4-dichloro-5-isopropyloxyphenyl-l,3,4-oxadiazolin-5-one (RP 17623) applied at 1 kg per ha was nonphytotoxic to directseeded rice and completely controlled all the annual weeds provided the rice field was not flooded too soon. RP 17623 has a long residual effect (about 6 months) compared to other herbicides used in rice.

Granular formulations of some toxic preemergence herbicides such as 2,4-D IPE (IPE ⁼ isopropyl ester) and 2-chloro-2',6'-diethyl-N-(butoxymethyl) acetanilide (CP 53619) also proved to be effective for use in directseeded flooded rice provided they were applied when the rice seedlings reached the 2 to 3 leaf stage (IRRI, 1971). The method was feasible because it took ⁵ to ¹⁰ days for the granular herbicides to become active in the soil (IRRI, 1970); and by the time they became active the rice seedlings were already big and resistant to the herbicides.

Very little attention, however, has been given to the study of weed control on directseeded nonflooded rice (upland rice), probably because this rice only makes up a very small percentage of total rice acreage in the world. The weed problem in upland rice is much more serious than in either transplanted or directseeded flooded rice, due

undoubtedly to the absence of flooding (IRRI, 1969). Low grain yields of upland rice are often attributed to the heavy infestation of both annual and perennial weeds.

Four chemical weed control methods have been suggested in controlling weeds in upland rice (IRRI, 1965). They are:

a. non-selective foliar herbicide application before planting or before rice seedlings emerge from the soil,

b. non-selective foliar herbicide application directly between rows after the rice seedlings have just emerged (upland rice is generally drilled-seeded 30 em apart),

c. post-emergence application of selective herbicides, and

d. preemergent application of selective herbicides.

Methods a and b are seldom successful because weeds grow between and within the row crop, and infest the soil before as well as after planting. Method c is expensive because there are no foliar herbicides which can kill both grassy and broadleaved weeds unless they are used in combination. Method ^d offers the best alternative since all types of weeds can be controlled in one application, and since preemergence herbicides are likely to be more selective than postemergence ones due to the deep placement of rice seed below the treated soil surface (IRRI, 1969). The most outstanding preemergence herbicide found by IRRI (1969, 1971) was CP 53619, an analog of propachlor. This herbicide gave excellent control of all annual weeds after a single application 2,4, or 6 days after sowing at 3 kg per ha. Propanil, which is widely used in South America for upland rice, failed to show sustained weed control. Other promising herbicides for upland rice included benthiocarb (IRRI, 1970).

Selectivity: A Basis for the Herbicide Application.

A herbicide application has selectivity when the weeds being treated are inhibited in growth or killed, while the crop remains relatively unharmed (Klingman, 1961). In crop management the aim of herbicide application is to kill as many weeds as possible without causing any permanent injury to the crop plants and without affecting its potential yield.

Herbicides can be divided into two major groups: (a) foliar applied herbicides which are predominantly applied postemergence, and (b) soil-applied herbicides which are mostly applied preemergence. The behavior and fate of these two major groups of herbicides are strikingly different as can be seen from Figure 1. However, for any herbicide to exert its toxic effects, it must undergo one or more of the following processes:

a. come into contact with the seed or parts of plants (leaves, stems, roots, etc.),

b. enter into plant via leaves, roots, or shoots,

c. translocate from site of absorption to site of toxic action, and

d. disrupt vital plant functions (e.g. photosynthesis, respiration, transpiration, and cell division and differentiation).

The differential amount of herbicide retained, absorbed, translocated, and remaining active to destroy vital functions of the plane will ultimately determine the degree of its selectivity. Each of these processes in effect can be changed by one or more factors relating to plant, herbicide, soil, climate, and method of application (Table 1). Thus a given herbicide is selective in a particular crop only within certain limits of environmental conditions, rate and method of

FI9URE 1. A SCHEME DESCRIBING THE FATE OF SOIL-APPLIED AND FOLIAR-APPLIED HERBICIDES IN THE SOIL AND IN THE' PIANT, RESPECTIVELY,

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TABLE 1. FACTORS KNOWN TO AFFECT HERBICIDE SELECTIVITY

(After Klingman, 1961; Holly, 1964; Wain, 1964, Ennis, 1964; Hammerton, 1966)

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application. Therefore, selectivity is relative; it is not absolute (Crafts and Ashton, 1970). Holly (1964), Wain (1964), Ennis (1964), Hammerton (1966) and Nangju (1970) have reviewed these factors in detail. Lange and Agama1ian (1970) have recently compiled the selectivity of 32 herbicides against 20 families of flowering plants.

In practice, selectivity can be achieved in two major ways:

a. the apparently resistant plant absorbs very little herbicide due to morphological and environmental factors (acquired selectivity).

b. the herbicide is well absorbed, but the resistant plants can detoxify it or the biochemical system inhibited in the sensitive plants are not affected in the resistant plant (inherent selectivity).

ACquired Selectivity. The killing effect of a herbicide is manifested only if the amount of the herbicide absorbed by plants has reached a threshold value, below which they will survive and above which they will be killed. This threshold value varies with the kind of herbicide used and with the age and type of plants. The amount of herbicide absorbed by the crops can be prevented from reaching the threshold value through various ways, without minimizing the intended weed control. In row crops directed spray of contact herbicides such as 1,1'-dimethyl-4,4'-bipyridinium ion (paraquat) and 2,2-dich1oropropionic acid (da1apon) is very common. The herbicide is applied only between the rows, thus killing the weeds in this zone and leaving the crop uninjured.

Deep seed placement is another possibility of reducing herbicide absorption by the crop (International Rice Research Institute, 1969). This technique works best if the herbicide is highly adsorbed by the soil and enters the plant primarily through the shoot. Knake, et al.

(1967, 1968); Prendeville, et al. (1967), Banting, et al. (1967, 1970), Appleby, et al. (1965), and Nishimoto (1970) found that some herbicides enter primarily through the shoot while others exert their phytotoxic effect mainly through the roots.

Granular herbicide formulations are often preferred to liquid formulations to control weeds in sensitive crops which have broad, succulent leaves. The granules can be broadcast directly on the soil without adhering to the leaves, while liquid formulations must be sprayed over the leaves, resulting in injury to the crop. However, de la Pena, et al. (1971) overcame this problem with taro (Colocasia esculenta) by pumping 2,4-dichlorophenyl p-nitrophenyl ether (nitrofen) in irrigation water. Using this method they obtained excellent weed control without any injury to taro.

Inherent Selectivity. The safest and the most practical way to obtain herbicide selectivity is to develop a herbicide which is inherently phytotoxic to weeds but not to the crop.

It has been frequently observed that many herbicides exhibit excellent selectivity although they are equally absorbed by both weeds and crops. Examples of this phenomenon can be found with propanil; 2-chloro-4,6-bis(ethylamino)-s-triazine (simazine); 2,4-D; MCPA; 2,4-DB; MCPB and 3-amino-2,5-dichlorobenzoic acid (amiben).

The mechanism of action of propanil in rice and barnyard grass has been described earlier.

Using intact plants Davis, et al. (1959) found that corn, cotton, and cucumber took up the same amount of simazine. However, approximately 95, ⁷⁵ and ⁵⁰ percent of it was converted to the hydroxy analogue by the three plants, respectively. Corn was quite tolerant, cotton was

moderately sensitive, and cucumber was very sensitive to simazine. It appeared that the rapid conversion of the chlorotriazines to the hydroxy analogues was the primary factor in the high tolerance of corn to simazine. However, Hamilton (1964) doubted whether such a relationship between degradation and tolerance was present in sorghum. Sorghum which was quite resistant to simazine was found to be lacking in benzoxazinone, and no conversion of the chlorotriazine to hydroxy derivative occurred.

2,4-D is very toxic to most broadleaves but not to grasses, except when they are applied at a very young stage. This differential tolerance is attributed to poor translocation of 2,4-D in grasses but not in broadleaves. Ashton (1958) found that both bean and sugar cane plants readily absorbed 2,4-D applied to their leaves, but that the bean plants transported the herbicide more readily.

Among the broadleaved weeds there is still differential tolerance of certain closely related plants to 2,4-D and this can be attributed to the oxidation of the acetic acid moiety. Luckwill and Lloyd-Jones (1960) observed that red currant, a 2,4-D-resistant plant, metabolized 50 percent of the side chain of 2,4-D in a week, whereas black currant, a 2,4-D-susceptible plant, broke down only 2 percent.

Most legumes are resistant to 2,4-DB and MCPB but are sensitive to 2,4-D and MCPA. The resistance of legumes to 2-4-DB and MCPB is due to the absence of beta-oxidase enzymes in their metabolic system. Weeds which have high amount of beta-oxidase enzymes are susceptible because they can convert herbicidally inactive 2,4-DB and MCPB to herbicidally active 2,4-D and MCPA, respectively (Wain and Wightman, 1954).

Amiben has been used quite successfully for preemergent control of weeds in soybeans. Colby (1966) suggested that the formation of N-glucosyl amiben from amiben and glucose in plants is probably a detoxification mechanism of the plant since he observed that amiben was translocated slowly in the resistant plants and most of it (about 90 percent) was converted to N-glucosyl amiben whereas in the susceptible plants the opposite occurred. His results were in agreement with Swan and Slife (1965) and Swanson, et al. (1966).

The Use of Adsorbents in Obtaining Acquired Selectivity

According to Upchurch (1966), the amount of soil-applied herbicide required for an eight-week period of weed control is A+B+CtD where:

 $A = kg/ha$ required to satisfy buffering capacity of the soil,

 $B = kg/ha$ broken down by microbial activity in eight weeks,

- $C = kg/ha$ lost in eight weeks through non-biological means (leaching, volatility, hydrolysis, etc.),
- $D = kg/ha$ required to provide the desired weed control effect at the end of the eight weeks (eight weeks period is assumed as the period for which critical weed control is required).

At time zero (i.e. at the time of herbicide application) the quantities $B + C$ and D will be available to plants, microbes, and other modes of loss. If the difference between time of planting and herbicide application is a matter of few days, quantities $B + C + D$ will also be available to crop plants. A sensitive crop plant will be killed unless this total amount is reduced to a level that will not cause any apparent injury. Reducing the herbicidal concentration can be done by applying an adsorbent around or above the crop plants or seeds. The adsorbent must adsorb the toxic chemical tenaciously, thus preventing it from coming into contact with any part of the crop plant. An

acquired selectivity will be obtained in this way provided the crop plants become more resistant to the chemicals as their roots penetrate the non-treated zone.

The above concept has been investigated by several workers since it was found ²⁴ years ago that activated carbon (an adsorbent) can deactivate 2,4-D (Lucas and Hamner, 1947). Ahrens (1964) and Sheets and Harris (1965) also reported that activated carbon broadcast on soil could reduce the waiting period normally necessary for planting a crop after herbicides which have long residual effects have been used, or to deactivate ^a herbicide if inadvertently applied to the wrong crops. Anderson (1968) calculated that 100 and 200 to 400 times as much charcoal as the herbicide were needed to deactivate a given amount of 3-(3,4-dichlorophenyl)~1-methoxyl-l-methylurea(linuron) and simazine, respectively. The degree of deactivation depends not only on herbicide type but also on dosage, plant species, and quantity of activated carbon applied (Bovey and Miller, 1969).

When activated carbon was incorporated in 1.5 ft. (about 0.5 m) bands above the row-seeded crop in a herbicide treated soil, crop protection was observed but there was poor weed control in the bands (Locascio, 1967). Linscott and Hagins (1967) improved this technique by applying activated carbon slurry in a much narrower band (2.5 cm wide) at the rate of 25 to 50 lbs. per acre (28 to 55 kg/ha) directly over the rows with alfalfa (Medicago sativa L.). In this way, alfalfa was found to be protected from 2-isopropylamino-4-(3-methoxypropylamino)-6 methylthio-s-triazine (G-36393) but not from 2-chloro-4-(ethylamino)-6- (isopropylamino)-s-triazine (atrazine). Burr, et al. (1972) also obtained good results with narrow bands of activated carbon.

The carbon applied at the rate of 130 kg/ha protected Italian ryegrass (Lolium multiflorum) seedlings from the toxicity of 3-(3,4-dichlorophenyl)-l,l-dimethylurea (diuron).

Band application of activated charcoal had several disadvantages. Apart from poor weed control in the bands, the material adhered tenaciously to equipment, clothing and the person, and a high amount of adsorbent was needed to get complete protection. Theoretically, 28 to 55 kgjha of activated carbon would be adequate but in practice, 192 kg/ha or more were needed to get a better protection, due to the effects of rain, soil and movement of herbicides (Linscott and Hagins, 1967). A further improvement of this technique was recently reported by Kratky and Warren (1971). They placed a mixture of activated carbon and vermiculate in a ratio of 5 to 3 in a hole 2 cm deep by 2.5 em diameter over cucumber (Cucumis sativus L.) and tomato (Lycopersicum esculentum Mill.) seeds, to the level of the soil surface. This mixture protected the seed from simazine, dimethyl tetrachloroterephthalate (DCPA), and nitralin provided the charcoal and the vermiculite were not blown away by the wind. This method was mechanized by making a wafer containing activated carbon, vermiculite, seed and fertilizers. Even then, this technique is only useful to expensive vegetable crops which do not require a lot of seed.

Ripper (1956) placed activated carbon in subsurface bands in the soil by special equipment to protect crop roots from damage by 2,3,6-trichlorobenzoic acid (2,3,6-TBA). Sufficient 2,3,6-TBA was intercepted by the charcoal band to protect crop roots.

As early as 1948 Arle, Leonard and Harris had noted that sweet potato sprouts could be protected from 2,4-D application by first moistening and then dusting their roots with activated carbon. Later Robinson (1965), Hughes (1964), Allot (1965, as cited by Andersen, 1968) and Kratky, et al. (1970) demonstrated that transplanted strawberry runners (Fragaria grandiflora Ehrh.) could be protected from simazine by dipping their roots in activated charcoal just before planting. Schubert (1967) reported that by dipping strawberry roots in dry activated charcoal before transplanting he not only obtained protection from simazine but also from 2,4-bis(isoproylamino)-6- (methylthio)-s-triazine (prometrYne); l-butyl-3-(3,4-dichlorophenyl)-1 methylurea (neburon); isopropyl m-chlorocarbanilate (chlorpropham); O,O-diisopropyl phosphorodithioate s-ester with N-(2-mercaptoethyl) benzenesulfonamide (bensulide); and 3,5,6-trichloro-o-anisic acid (tricamba). Root dipping is now practiced widely by strawberry farmers in England because there is as yet no herbicide which is completely selective for this crop. However, the practical value of root dipping is limited to vegetable crops transplanted in upland soil. In transplanted rice which grows in water, the charcoal applied to the root region will obviously disperse in water, and will not protect the crop.

There is still another possible technique which can be used to protect the crop from herbicide application; coating the crop seed with an adsorbent such as activated carbon. The adsorbent will deactivate the herbicide around the seed, thus allowing it to germinate and grow. The technique is simple and cheap and allows effective weed control beyond the treated seed. A preliminary study conducted by the International Rice Research Institute (1969) indicated that seed coated with activated carbon was remarkably protected against the lethal effects of CNP, dichlobenil, NC-5024 and pyrichlor. However, the method required rather precise land levelling and water management. The carbon easily dispersed in the water-saturated rice-field because an adhesive was not used. Further studies are needed to overcome these problems and to improve the technique.

Very recently Burnside, et al. (1971) were able to protect corn seed (Zea mays, L.) from high concentrations of S-ethy1 dipropy1thiocarbamate (EPIC) by dusting the seed with 1,8-naphtha1ic anhydride. At 0.5% by corn seed weight, the compound eliminated most of the corn yield loss caused by EPIC at 3.4 to ¹⁰ kg/ha. However, it is not known how 1,8-naphthalic anhydride protects corn seed from EPIC.

Seed pe11eting has been utilized by Australian and New Zealand workers in their attempts to solve the problem of pasture establishment in acid soils (Bergenson, et al., 1958; Cass Smith, 1959; Hastings and Drake, 1960; Thompson, 1962; Lobb, 1958). They solved this problem by coating the inoculated seed with lime or dolomite using methyl cellulose or gum arabic as an adhesive. The coated, inoculated seed can be mixed with superphosphate prior to seeding without injury and can be stored for a short period of time before planting (Norris, 1967). P1ucknett (1971) has reviewed this subject in his recent paper.

Numerous uses of seed pe1leting have been cited by several workers. Seed pelleted with insecticides or fungicides has been used to repel or control specific pests (Russel, Coa1drake and Sanders, 1967; Brockwell, 1963). Seaman and Brandon (1970) have attempted to coat rice seed with various inert materials such as kaolin, bentonite and talc to add weight

and thus eliminate presoaking seed before it is broadcast on flooded soil. Uncoated seeds often float when broadcast in a flooded rice-field since they are very light.

Hacker (1969) pelleted sorghum seed with stearic acid and shellac in an attempt to delay sorghum establishment until ideal soil moisture conditions existed.

Lettuce seed encapsulated in pressed vermiculite tablets or claycoated seed can facilitate precision placement of machine planted seed in desert areas of California (Robinson and Johnson, 1970).

Crocker and Barton (1953) suggested incorporating plant growth regulators in the pellet to promote rooting and hasten emergence of the seedlings. Finally, pelleting can also make small seeds larger and heavier thus permitting foresters to reseed prairie lands and forests (Rudolf, 1949 as cited by Plucknett, 1971).

It is evident from the above review that pelleting seed with chemicals or substances can help solve several problems that often exist during crop establishment.

The Uptake of Herbicide by Seeds.

Mitchell and Brown (1947) reported that both fully swollen and unswollen mustard (Brassica sp.) seed absorbed considerable amounts of 2,4-D from aqueous solutions. They also found that dormant imbibed seed of subterranean clover (Trifolium subterranean L.) planted in soil containing 2,4-D germinated without injury when their dormancy was broken after degradation of 2,4-D.

It is now known that herbicide absorption by seed is largely ^a physical process since both living and dead seed show similar absorption
rates which are not associated with imbibition of water (Rieder, et al., 1970). Rieder, et al. (1970) also found that diffusion, rather than mass flow, was an important mechanism of herbicide transport to the seed. They found after 48 hours of seed-herbicide contact that the ratios of herbicide concentration in the water contained in the soybean to the concentration of the herbicide in the aqueous solution surrounding the soybean seed were 3.0, 6.7, 27.8, 36.4 and 68.5 for amiben, atrazine, linuron, EPTC, and ch1orpropham, respectively. It appears that seed acted as perfect "sinks" for ch1orpropham, EPTC and 1inuron but not for amiben and atrazine. The seed was considered to be a "sink" if diffusion in seed was much faster than in soil (Scott and Phillips, 1971).

Concentration of the herbicide within the seed with time and distance where the movement is in a radial direction can be described by Fick's second law (Moore, 1962). Using this formula Scott and Phillips (1971) were able to calculate the amount of chlorpropham taken up by soybean from aqueous solution as a function of time. They found that the predicted values agreed very well with the observed values in both presoaked and not presoaked seed of soybean. They also found that the concentration of the herbicide in the seed increased as seed size decreased.

Physico-chemical Properties of Adsorbents.

The amount of adsorbent which can be pel1eted around the seed is relatively small, a matter of a few mg. Thus an adsorbent which has extremely high adsorption capacity for a wide range of herbicides is highly desirable for effective pe11eting material. Such an adsorbent, if available, must be relatively cheap and accessible to farmers.

Robinson (1965) compared six adsorbents in their efficiency to protect newly planted strawberry runners and found that powdered steamactivated charcoal was the most suitable, followed by powdered vermiculite, kieselguhr (siliceous deposit occurring in Northern Ireland), dried manure, and dried grass. Jordan and Smith (1971) showed that activation of charcoal was necessary for adsorption to occur. Wood powder and animal powder (both non-activated charcoals) adsorbed only 4 mg/g of atrazine compared to MCP Petroleum Base, Norit A alkaline, Witco 249 and Nuchar C-190-N which adsorbed 366 to 485 mg/g of atrazine.

Coffey and Warren (1969) measured biological activity of several herbicides in adsorbent-containing silica sand using sorghum and cucumber as test plants. They concluded that activated carbon was generally 10 to 100 times more efficient in reducing phytotoxicity of herbicides than other adsorbents such as bentonite clay, finely ground muck soil, anion exchange resin, and a cation exchange resin. Exchange resins were quite efficient for some herbicides which showed pronounced positive or negative charges. However, they are expensive and hence have rather limited practical usage in seed pe11eting. Grover (1971) reported that activated carbon was the best adsorbent commercially available today. He found that the decreasing order of adsorption of 4-amino-3,5,6-trich1oropico1inic acid (picloram) by adsorbents was activated carbon, anion exchange resin, peat moss, cellulose triacetate and cation exchange resin.

There is no clear explanation regarding the mechanism of adsorption of activated carbon or activated charcoal. The tremendous capacity of activated carbon to adsorb ^a wide range of herbicides makes it an

interesting and useful material in seed pelleting material. Activated carbon behaves somewhat like organic matter in that its adsorption capacity is dependent upon surface area, temperature, pH, and the physico-chemical properties of the adsorbates.

Coffey and Warren (1969) found that the greater the surface area of the carbons, the more efficient they were in adsorbing herbicides. Darco G-60, a highly purified and fine activated carbon, was the most efficient, followed by Hydro Darco-B, Darco-M, Darco 8-51 and Darco KB. The surface area of these carbons vary from 600 to 1200 m^2/g .

A change in temperature may increase the adsorption of one compound on carbon and simultaneously decrease the adsorption of another in the system. The variable effect of temperature on adsorbabi1ity of activated carbon was due to indirect effect of temperature on solubility and volatility of adsorbates (Hassler, 1963). Weber (1965) reported that both 6,7-dihydrodipyrido (1,2-a:2,1-c) pyrazinediium ion (diquat) and paraquat were adsorbed considerably greater by carbon (Darco G-60) at 55^oC than at 10^oC. However, the adsorption of 2,4-bis(isopropylamino) -6-methoxy-s-triazine (prometone) on carbon was the same at both temperatures.

Yamane (1968) and Ward and Getzen (1970) demonstrated the effect of pH on the adsorption of aromatic compounds on activated carbon. Lowering the pH from 11 to 3 increased the adsorption of 2,4-D, amiben and 3,6-dichloro-o-anisic acid (dicamba) by activated carbon (Ward and Getzen, 1970). Maximum adsorption was attained near the point where $pH = pKa$. The pKa values of 2,4-D, amiben and dicamba were 3.3, 3.4 and 1.9, respectively. However, adsorption of 2-(ethylamino)-4- (isopropy1amino)-6-methy1thio-s-triazine (ametryne) on activated carbon was reduced by lowering pH from 7.1 to 4.1 (Yamane, 1968). The pKa value of ametryne was 4.0. Lowering pH of the solutions decreased dissociation of amiben, 2,4-D and dicamba CWard and Getzen, 1970) but increased the dissociation and solubility of ametryne and atrazine (Yamane and Green, 1972). Thus, it appears that changes in pH, which increase or decrease dissociation and/or solubility of the adsorbate, may reduce or enhance adsorption of herbicides on activated carbon. Herbicide adsorption on activated carbon was highest when the herbicide was in the molecular form (Anderson, 1947).

An increase in solubility often results in greater affinity between the solute and the solvent, and acts to oppose the attraction exerted by the charcoal. Leopold, et al. (1960) studied the relationship between solubility and adsorption of 17 chlorinated derivatives on charcoal, and found that there was a strong inverse correlation between the adsorption and solubility. Phenoxyacetic acid was most soluble and least adsorbed of the series. Successive chlorination in the phenyl ring decreased solubility and increased adsorption on charcoal. However, solubility acts only as a restraining force, a brake against the pull of the charcoal (Hassler, 1963). That is to say that even great solubility does not prevent adsorption of a substance that is strongly attracted to the carbon surface.

Hassler (1963) reported that physico-chemical properties of the adsorbates such as molecular size, dissociation constant, nature of substituent groups, and molecular structure also influenced adsorption at the carbon-liquid interface. An increase in size of the solute molecule usually favored adsorption. On the other hand, dissociation

was adverse to adsorption by carbon. Strongly ionized salts were not adsorbed in appreciable quantities whereas organic acids and bases were well adsorbed.

Substituent groups of organic compounds influence the adsorbability of carbon in aqueous solution. Hydroxyl, amino and sulfonic groups are generally more attracted to the carbon surface than nitro, carbonyl and halogen groups (Hassler, 1963).

Spatial arrangements of atoms and group in a molecule influence adsorbability of carbon, and the effect of a substituent is modified according to the position occupied (Hassler, 1963). Aromatic compounds for instance, are in general more adsorbable than aliphatic compounds of similar molecular size. Branched chains are usually more adsorbable than straight chains, while optical isomers (dextro and leva) are equally adsorbed. The above deductions are, however, based on limited data.

CHAPTER III. MATERIALS AND METHODS: GENERAL ASPECTS

Field Experiments

Field experiments were conducted at the Paddy-Crop Experiment Station located in Wailua valley, Kauai. This taro and rice research center is part of the Hawaii Agriculture Experiment Station in Kauai. The area is bounded by Sleeping Giant mountain and Opaekaa stream. The main source of irrigation water is from Opaekaa falls located about two miles up stream from the station. Occasional heavy rains normally flood the whole valley up to 1 m deep. The annual rainfall is approximately 55 inches (139.7 cm) and the elevation is less than 5 feet (1.5 m).

The list of common weeds found at the Paddy-Crop Experiment Station is given in Table 2. Of these weeds Echinochloa crusgalli, Jussiaea suffruticosa, Cyperus difformis and Ceratopteris siliguosa are most common in the lowland (flooded) soil, while Echinocloa crusgalli, Echinocloa colonum, Eleusine indica, Amaranthus sp., Eclipta prostrata and Portulaca oleracea are most widespread in upland (nonflooded) soil. Monochoria yaginalis (pickerel weed), a very common broadleaf weed in rice fields in tropical Asia, is conspicuously absent in this area but not in other parts of Kauai. The weed population density in lowland soil is seldom uniform, hence Echinocloa crusgalli seed obtained from the International Plant Protection Center in Corvallis, Oregon, is normally broadcast on puddled soil prior to sowing and/or herbicide application in order to obtain uniform growth of grassy weeds. This particular barnyardgrass, however, differs from native species in being generally short, fast growing, and by dying after reaching flowering stage.

TABLE 2. COMMON RICEFIELD WEEDS IN WAILUA, KAUAI

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TABLE 2. (CONTINUED) COMMON RICEFIELD WEEDS IN WAILUA, KAUAI

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Birds are of special interest from the point of view of their damage to rice plants. Directseeded rice has a special problem in this area because birds can destroy it right from sowing up to harvesting stage. There are at least **¹¹** species of bird observed in Wailua valley (Table 3). According to Munro (1960) and Hawaii Audobon Society (1971) not all of these birds are native to Kauai. Many of them were introduced about a hundred years ago, while others are classified as migratory birds. The most troublesome birds to directseeded flooded rice are wild ducks, American coot, ring-necked pheasants and rice birds. The first three birds can either eat rice seed or destroy young rice seedling. The last birds are harmful to all types of rice and other cereal crops since they eat the soft grains at milky or soft dough stages. Because of this, directseeded rice can never be grown in this area unless the whole field is enclosed with a strong and bird-proof net from just before sowing until harvesting stage.

Description of Hauula paddy soil. The soil throughout the Paddy-Crop Experiment Station is a member of very fine, oxidic, non-acid, isohyperthermic family of Typic Fluaquents. It is an Entisol. Its proper name is Hauula Paddy soil belonging to Hanalei series. The soil is formed from sediments deposited by the Wailua river as well as Opaekaa stream, and from materials washed down from the slopes of the surrounding mountains. This alluvium is in fact deposited over peat and muck.

The soil profile is typical of those poorly drained lowland soils. The water table is present at about 40 cm. The A horizon is generally very dark to grayish-brown, silty clay to clay with common fine prominant

TABLE 3. COMMON BIRDS OBSERVED AT PADDY-CROP EXPERIMENT STATION, WAILUA, KAUAI

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yellowish-red and dark reddish-brown mottles. The B horizon is very dark gray, silty clay to clay with fine yellowish-red to black mottles, massive, and sticky and plastic when wet. The C horizon, found 50 to 160 em deep, is composed of black peat and muck.

Some of the physical and chemical properties of the top 15 cm of the soil are shown in Table 4.

Briones (1963) and A1cordo (1963) have studied the physical and mineralogical properties of Hauula Paddy soil. Their data showed that the organic matter content of the soil was generally higher in the wet paddies (flooded rice soil) than in the reclaimed area, and in the top soil than in the subsoil. Because of its high organic matter and clay content the soil is very difficult to work with when it is dry. The soil easily cracks into big crumbs upon slight drying owing to the nature of the clay minerals. The main clay minerals are kaolinite and halloysite (personal communication with Dr. Goro Uehara).

Characteristic of the rice variety used. The only rice variety used throughout the study was IR8, a high-yielding variety developed by the International Rice Research Institute in Philippines. This variety is characterized by its dwarf stature, stiff straw, erect leaves, high tillering ability, high seedling vigor, responsive to nitrogen fertilizers and highly resistant to lodging (International Rice Research Institute, 1967). It is insensitive to photoperiodism, and hence can be grown anytime of the year provided temperature is not limiting. Its growth duration is about 125 to 130 days. IR8, however, has lost its popularity since IR 20 and IR 22 were released in 1970 (International Rice Research Institute, 1971). The latter varieties have much better

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cooking and eating qualities while still retaining most of the excellent characteristics of the former variety,

Properties of the main herbicides studied. There were more than 20 herbicides used in this study but only three of them were studied in detail. These were amiben, CP 53619 and RP 17623 which represent a wide spectrum of toxicity to directseed rice. Their chemical and physical properties are shown in Table 5.

Amiben is highly toxic to directseeded flooded rice. According to Obien, et al. (1970) amiben was rather selective to transplanted rice up to 6 Ib per acre (6.72 kg/ha) but the rice seedlings showed some injury even at 2 lb per acre (2.24 kg/ha), On the other hand, CP 53619 was only slightly toxic to transplanted rice (International Rice Research Institute, 1968 and 1969). Attempts to develop this herbicide for directseeded flooded rice have not been successful, When it was applied three or four days after sowing before the weeds have emerged the rice seedlings were often killed (Unpublished data of the multicrop screening trial by the International Plant Protection Center in ¹⁹⁷⁰ and 1971 in Wailua, Kauai), On the other extreme of toxicity, RP 17623 was shown to be very selective to directseeded flooded rice at lIb/acre (1,12 kg/ha) provided the field was not flooded too soon after the application (Obien, et al., 1971; Smith and Fox, 1971). In this study RP 17623 was used at high rates (3.36 to 4.48 kg/ha) to determine whether the adsorbent-coated rice seed was effective in minimizing phytotoxicity.

All of the three preemergent herbicides discussed above controlled most of the annual weeds effectively when applied before or just after

TABLE 5. CHEMICAL AND PHYSICAL PROPERTIES OF AMIBEN, CP 53619 AND RP 17623.

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the weeds emerge. Amiben has been used for soybean and other crops for some time, but the other two herbicides are still in the development stage. However, they have proved to be promising in the herbicides trials conducted in the United States, Philippines and elsewhere.

Land preparation. The experimental fields were prepared with handoperated paddy tractors. These tractors did both the ploughing and harrowing. The field was harrowed several times until the weeds, rice straw and other stubble had been incorporated into the soil, the land was well puddled, and mud and water were thoroughly mixed. After that the field was properly levelled with a long board to allow uniform drainage and irrigation water distribution. Two or three days later, when the mud had settled down, small levees (15 em high and 20 em wide) were constructed by hand so as to separate the herbicide treatments between. two adjacent plots. Levee building was laborious and timeconsuming. For this reason galvanized metal· sheet squares with a dimension of 1.2 m by 1.2 m and a wall of 15 cm high were used in some field experiments. The metal sheet squares effectively prevent herbicide movement from one plot to another. Herbicides can be applied accurately in these small plots but unfortunately no reliable grain yield data can be obtained owing to a small sampling size.

Method of planting and herbicide application. Before or after the land preparation, but not after sowing, all the experimental fields except the bird repellent experiments were enclosed with a strong, bird-proof net in order to protect rice from birds at seedling establishment as well as ripening stages. Except for the preliminary experiment, all rice seed was pregerminated before broadcasting by hand on well-drained, puddled soil. Pregermination was done by soaking

seed in water for 24 hours followed by 36 to 48 hour incubation. Carbon pelleting was also done on pregerminated seed. Before pelleting the seed, activated carbon Darco-G-60 and polyvinyl acetate (PVA, commerical preparation of Elmer's glue) were measured. For every 1 kg of rice, a total of 450 g activated carbon and 150 ml 50% PVA was used in making triple-carbon-coated rice seed. Detailed procedure of seed pelleting is described in Chapter VI.

Method and time of herbicide application depended on the herbicide formulation used in the experiment. The liquid herbicides were generally applied at sowing using a C02-pressurized hand spray boom (pressure 25 to 30 psi, nozzle size 8003). The granular herbicides were broadcast by hand either before or after sowing. Calibration, cleaning of spray boom, order of herbicide application and other precautions strictly followed the procedures described by Furtick and Romanowski (1971).

The whole processes from harrowing, land levelling, levee building/ placement of metal squares, soaking, incubation, seed pelleting, sowing to herbicide applications had to be carefully synchronized so that no delay was made in carrying one operation to the next. This was very important since improper time of sowing or herbicide application could seriously affect experimental results.

Crop management. It takes at least ¹²⁵ days for IR8 to mature. During its growing period the crop had to be looked after so that environmental factors would not upset the treatment effects. The four aspects of crop management which were of utmost importance were water management, fertilization, insect and disease control, and weed control outside the treated plots.

Water management of directseeded flooded rice was very crucial to the survival of carbon-coated rice seed; hence extreme care was exercised during the first two weeks after sowing. The field was kept unflooded but moist at sowing until after the seedlings reached 2 or 3-leaf stage. The water was then slowly introduced to a depth of 2-3 em. The depth of water was gradually increased to 5-10 em as the plants grew taller. The field was again drained completely about two weeks before harvesting for grain yield. The crop was usually harvested about 30-35 days after flowering.

Since flooded rice in Paddy-Crop Experiment Station showed notable responses only to nitrogen and phosphorus (unpublished data of Dr. Ramon de la Pena) only these two nutrients were added to soil in the form of urea, ammonium phosphate and/or triple super phosphate. The rates of fertilizer application were 150 kg N and 100 kg P per ha for summer maturing crops, and 100 kg N and 100 kg P per ha for crops maturing either in spring or fall. The upland rice, however, received an extra of 200 kg P and 100 kg K per ha. Most of them were applied just before the last harrowing so that they could be incorporated in the soil.

Fortunately, rice diseases did not present any problem in Kauai. Some insects did cause a problem to rice plants. These were stripedstem borer (Chilo suppresalis), Chinese grasshopper (Oxya chinensis), and long horned grasshopper (Conocephalus saltator). Other insects such as southern green stink bug (Nezara viridula) and mole cricket (Gryllotalpha africana) were only seen occasionally. Insect control was carried out by applications of diazinon (O,O-diethyl O-(2-isopropyl-6 methyl-4-pyrimidinyl) phosphorothioate) and naled (1,2-dibromo-2, 2-dichloroethyl-dimethyl-phospbate).

The weeds growing around the experimental fields, on the inside levees and the canals were frequently handweeded or sprayed with paraquat. Weedy fields tended to attract high population of grasshoppers.

Data collection. During the first three weeks after sowing the percentage survival of plants from both coated and uncoated seed were recorded. These data were best taken when the rice had not tillered. ^A seedling was considered viable when it was still standing in the soil at 14 days after herbicide treatment. A quadrat measuring 40 by 50 em was used to count the number of seedlings per square meter. The same quadrat was used to count the number of tillers and panicles (reproductive tillers) per square meter.

Plant height at different stages, toxicity and weed control ratings and yield components data were also collected. Toxicity and weed control ratings were visually evaluated by comparing the treated plots with the controlled plots.

Grain yield data were obtained by taking one-square-meter samples using a 80 em by 125 em quadrat. The samples were threshed, cleaned, and then dried for two days at 60 C. The results were converted to yield of unhulled rice at 14% moisture in kg per ha.

All the pertinent data were analyzed statistically. When the F tests were found significant, LSD values at 1 or 5% were computed to compare the treatment means. According to the latest study by Carmer and Swanson (1971) the use of a preliminary F test with the least significant difference (FLSD), Duncan's multiple range test and a relatively new Baysian modification of the least significant difference are more appropriate for use in research than the ordinary least

significant difference (LSD) and Tukey's significant difference (TSD or HSD). FLSD was preferred in this study due to its familiarity to researchers and its simplicity of application.

Crop weather 1970-1972*. At the beginning of the year (January and February) the temperatures were generally low, daylength was short, and total rainfall per week was high, resulting in low solar radiation during this period (Figures 2 and 3). The mean low and high temperatures during these two months were about 60 and 78° F, respectively. The average temperatures increased and reached their maxima in July and August. The longest daylength (S09 minutes), however, occurred in June-July. The solar radiation rose from about 2000 gca1/em/week in the winter up to about 4000 gcal/em/week in July and August. Solar radiation and temperature readings began to decrease again in September and reached their lowest values in January.

Rainfall appeared to be well distributed throughout the year although most of the heavy rainfall occurred primarily in winter. Where total rainfall per week exceeded 80 mm, flooding invariably occurred in Wai1ua valley. The floods in 1970 took place in November, in 1971 in March and December, and in 1972 in January, February and April. These unpredictable rains accounted for most of the variations in the results obtained from the field experiments.

Pot Experiments

Pot experiments were conducted at the greenhouse of the main Hawaii Agricultural Experiment Station in Wai1ua, Kauai, using the same soil

^{*}The author is very grateful to the Lihue Plantation Co., Ltd. and the National Weather Service of the Department of Commerce for making available their weather data, especially on solar radiation and day1ength.

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as for the field experiments. Most of these experiments were conducted with yellow, plastic pots having inside dimensions of 27 and 30 cm, and a depth of 13 em. Each of the pots was filled with 20 lb (9kg) puddled soil, and fertilized with ammonium phosphate fertilizer. The pots could be surface-irrigated to a depth of at least 5 em.

The upland rice experiments were conducted in different pots since the above pots did not have holes at the bottom to provide drainage. For this purpose I-gallon cans (18 em high and 15 em in diameter) or rectangular metal cans with inside dimensions of 33 em and 50 em and 10 em deep were used.

In most cases, the coated and uncoated rice seeds were pregerminated before sowing them in the pots to insure at least 95% survival if no herbicide was applied. The pregerminated seed was selected for uniformity in radicle and co1eopti1e length. Before sowing the seed the soil in the pots were thoroughly levelled and smoothed down with a piece of plastic. Rice seed was planted in rows with 5 to 10 seeds per row depending on the objectives of the experiments.

Liquid herbicides were applied with a C02-pressurized hand spray boom by reducing the number of nozzles to 2 or 1 depending on the size of the pots. Herbicide application with a pipette was discouraged since it was found that for uniform application throughout the soil surface, a large amocnt of water was needed, and high volume applications generally were found to increase the toxicity of herbicides to rice seed. The granular herbicides were usually broadcast by hand.

During the duraction of the experiment watering of pots and insect control (especially against mites) were regularly carried out

depending on the need. Mites were easily controlled with kelthane (1,I-bis(chlorophenyl)-2,2,2,-trichloroethanol).

Most of the greenhouse experiments were harvested 5 to 6 weeks after sowing. Data on percentage of survival of seedlings, plant height, number of tillers per plant and fresh weight/dry weight were collected from each experiment.

Laboratory Experiments

Before greenhouse or field experiments were carried out some urgent information was often needed to answer specific questions so that effort, time and money were not wasted. This information was normally obtained by conducting short experiments in the laboratory using petri dishes, paper cups or sophisticated equipment, such as the UV spectrophotometer.

Germination and seedling growth tests were conducted on petri dishes which were either placed in a dark germinator or a growth chamber. Most of the germination problems encountered in the field were solved in this way in the laboratory. Problems relating to pelleted seed were also solved first in the laboratory in order to find the most stable coatings of high quality. The adsorption capacity of the adsorbents, the site of uptake and leaching characteristics of the main herbicides used, and herbicide diffusion to coated and uncoated rice seed were also studied in the laboratory to explain the results obtained in both the greenhouse and the field. The detailed procedures of all these experiments were described in Chapters ^V and IX.

CHAPTER IV. PRELIMINARY STUDY ON SEED PELLETING

Very little is known regarding the use of pelleted seed as an aid to seedling establishment in directseeded rice, especially in soil treated with toxic herbicides. The only information available on this subject is a field experiment conducted by the International Rice Research Institute in 1969 to test the efficiency of activated carbon coatings in protecting directseeded flooded rice from toxic preemergence herbicides (International Rice Research Institute, 1970). Although the results of this experiment were promising, there is a great need for improvement in order to make the technique work under ordinary farm conditions.

The first step in developing an effective pelleting technique is naturally to identify field problems which may be encountered with the use of pelleted seed. Having identified these problems, the next step would be to solve them using all the available means, bearing in mind that the technique should be kept as simple and as practical as possible in order to be acceptable to farmers.

Problem identification was the primary objective of this experiment. The direction of the future work was based on the outcome of this study.

MATERIALS AND METHOD S

Rice seed (Oryza sativa, var. IR8) was soaked overnight and then pe1leted with activated carbon Darco G-60 using 45% gum arabic as an adhesive. Darco G-60 was selected because it was the most effective activated carbon found by Coffey and Warren (1969). The adhesive was added to hold the carbon to the seed when both of these were mixed in a container. Sufficient adhesive was added to just coat the seed. Too much adhesive necessitated the addition of an excessive amount of carbon to break the lumps of seed. After coating, the coated rice was dried for a few hours in the shade.

A few days before pe11eting rice seed with activated carbon, the rice field was properly puddled and levelled with hand-operated paddy tractors. The size of the experimental field was ¹⁴ by ³⁹ ^m and it could accommodate at least 96 galvanized metal squares measuring 1.2 by 1.2 m. The squares were spaced 1.7 m apart. The design of the experiment was split plot. Two squares were placed side by side to form a subplot which received the same herbicide treatment. The subplot treatments were uncoated and carbon-coated rice seed which was broadcast at the rate of 100 kg/ha. The main plot treatments consisted of 10 herbicides (4 emulsifiable concentrate, 4 granular and 2 wettable powder formulations) and 2 controls (handweeded and unweeded controls). All the treatments were replicated four times.

The ten herbicides used were 2,4-D IPE, amiben, AN 56477, MBR 4400, RH 892, HOE 2933, trif1ura1in + 2,4-D, nitrofen and 2-(3,4-dich1oropheny1)-4-methy1-1,2,4-oxadiazo1idine (bioxone). Amiben was applied as granules and also as liquid. The coded compounds AN 56477, MBR 4400, RH ⁸⁹² and HOE ²⁹³³ were still at development stage but they looked very promising in the screening trials conducted by the International Plant Protection Center and Kauai Branch Station in the Paddy-Crop Experiment Station. Their chemical structures were unknown. All the herbicide used in this study were known to be toxic . to directseeded, flooded rice.

Both coated and uncoated seed were broadcast on August 16, 1970. They were treated with herbicides a day after sowing (DAS). The field was flooded a week after sowing. About 30 DAS visual ratings on crop stand, herbicide injury and weed control were taken.

RESULTS AND DISCUSSION

The experimental procedure described above was actually a second attempt to establish directseeded rice using activated carbon coatings. The first experiment was conducted two weeks earlier when the weather was hot and dry. Rice seed (Oryza sativa, var. Caloro) broadcast on the surface of puddled, non-flooded soil germinated very poorly on exposure to intense sunlight during the day. The soil dried up and began to crack three days after sowing. There was uncertainty whether to irrigate the field or not. Flooding the field at this time would increase herbicide toxicity to germinating rice seeds, while no irrigation would reduce percentage of germination. When it was finally irrigated, it was too late to save the seed. The controlled plots showed only 40-47% germination. The experiment was repeated by moving the galvanized squares to untreated soil adjacent to the squares. This was possible since the distance between two squares was 1.7 m, and the size of the metal squares was only 1.2 by 1.2 m.

Excellent germination of rice seed obtained in the second try was attributed to frequent rains occuring during the first week after sowing. However, these rains greatly dispersed the carbon coatings around the rice seed, resulting in severe phytotoxicity to rice seedlings observed in most of the treated plots. Gum arabic seemed to be a poor adhesive for seed pe11eting. According to Brockwell (1963) gum arabic was

better than methyl ethyl cellulose since, besides providing a strong pellet, it improved rhizobia survival in storage after inoculation of legume seeds.

The results shown in Table ⁶ indicated that there was only little success with carbon-coated seed. Although the crop stand of coated seed was slightly better in some plots (e.g. 2,4-D IPE, amiben, MER 440, RH 892, AN 56477 and HOE 3922) compared to that of uncoated seed, both seeds suffered about the same magnitude of phytotoxicity. Seedlings treated with amiben, 2,4-D IPE and RH 892 floated in water during the first two weeks after treatment since the herbicides caused severe root inhibition. Most of the injured seedlings, however, recovered after a few weeks. At 75 DAS there were only slight differences between the heights of treated plants and those of controlled plants. Plate 1 shows the stand and growth of seedlings from carbon-coated and uncoated seeds which were treated with AN 56477.

Another problem observed in this experiment was the poor performance of all the applied granular herbicides except amiben, under the conditions that were intended to favor the growth of seedlings from carbon-coated seed from toxic herbicides. If the coated seeds were sown in water, the herbicides would have killed the germinating rice seed more readily than if seeding was done on non-flooded soil. Soil water content plays an important role in increasing or decreasing herbicide toxicity to plants (Green and Obien, 1969; Jordan, et al., 1968; Stickler, et al., 1969). Granular formulations of bioxone, nitrofen and trifluralin + 2,4-D did not control weeds at all, and both coated and uncoated rice seed growing on these plots showed no apparent injury. Obviously these herbicides were ineffective when they were

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TABLE 6. EFFECT OF SEVERAL PREEMERGENT HERBICIDES ON THE SURVIVAL AND GROWTH OF SINGLE CARBON-COATED RICE SEED USING GUM ARABIC AS AN ADHESIVE

*Stand Rating: $10 = \text{exce}11$ ent stand, $0 = \text{bare} \text{so}11$ **Toxicity Rating: ¹⁰ = complete kill, 0 = non-phytotoxic ***Weed Control Rating: 10 = complete control, 0 = no control a_U = Uncoated Rice Seed $bC =$ Carbon-Coated Rice Seed

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PIATE 1. GENERAL VIEW OF THE PRELIMINARY FIELD EXPERIMENT IN WHICH GALVANIZED METAL SQUARES WERE ARRANGED SIDE BY SIDE TO FORM SUBPLOTS. IN THE FOREGROUND SINGLE CARBON-COATED SEED WAS BROADCAST ON THE LEFT SQUARE AND UNCOATED SEED ON THE RIGHT SQUARE. BOTH OF THESE SQUARES WERE TREATED WITH AN 56477.

applied on non-flooded soil. Water was needed to dissolve and distribute the herbicides. Experiments using granular herbicides conducted in the Philippines suggest that the field should be flooded continuously for about 7 days for effective weed control (International Rice Research Institute, 1969). Both liquid and granular amiben worked equally well in controlling most of the annual weeds under these conditions.

Some of the barnyard grasses located near the carbon-coated seed survived even though they were treated with herbicides. This was observed in plots treated with AN 56477 and HOE 2933. Apparently, the carbon dispersed from the rice seed was able to protect the barnyardgrass seed from toxic herbicides.

SUMMARY AND CONCLUSIONS

The easiest and simplest approach in obtaining herbicide selectivity with adsorbent-pelletted rice seed is to broadcast the seed on nonflooded, puddled soil when there is an intimate contact between adsorbent and herbicide, and greater chance of survival of rice seed due to the absence of standing water. This approach, however, suffers from one main drawback: poor germination of rice seed. Good germination is undoubtedly the key to the good seedling establishment. Without it, all would fail inspite of the effectiveness of the pelleting technique. Therefore, the first problem was to devise ways of obtaining excellent seed germination, independent of rainfall and/or early irrigation.

The second problem was to find a nontoxic adhesive which will give stable coatings even under rainfall conditions. Any adhesive

will not do, as was shown by the poor performance of gum arabic. The unstable coating of gum arabic was partly responsible for the severe injury of carbon-coated seed and the survival of weed seed located near the coated seed. The high toxicity of carbon-coated seed could also be due to an inadequate amount of carbon applied around the seed. Herbicide phytotoxicity was inversely correlated to the quantities of activated carbon applied (Jordan and Smith, 1971; Linscott and Hagins, 1967). The rate of activated carbon application per unit area can be increased by increasing the number of coating layers on the seed, by increasing the seeding rate of coated seed, or both.

Early flooding and late flooding of the field were equally bad for seedling establishment. Early flooding increases herbicide toxicity, while delayed flooding reduces percentage total emergence of rice seedlings due to lack of water. The problem of determining the optimum time of flooding is equally important from this viewpoint.

Granular herbicides obviously have to be handled separately from liquid materials since the two groups of herbicides behave differently in soils. The former works best in flooded soil while the latter performs well even though the soil is only saturated with water. A special water management has to be worked out for granular herbicides to obtain both excellent weed control and high percentage of survival of coated seed.

CHAPTER V. FACTORS AFFECTING GERMINATION AND SEEDLING ESTABLISHMENT OF RICE

(Oryza sativa L., var. IR8)

The process of germination can be divided into four stages (Heydecker, 1956): (a) germination, involving the inception of rapid metabolic activity within the seed, and the appearance of first radicle and then the aerial parts, (b) underground elongation of the seedlings which relies on its food reserves, (c) emergence of the aerial parts from the soil, and (d) the beginning of the photosynthesis process which results in dry-weight increases in the plant.

Various factors affect the germination of seeds. Crocker and Barton (1953) and King (1966) have reviewed these factors in detail. Seed maturity, temperature, soil moisture, soil aeration, depth of seed burial and presence of toxic substances or gases around the seed are common factors shared by most seeds. Some seeds, however, have additional requirements for germination. These requirements may include soil pH, light, alternate wetting and drying of the soil surface and disturbance of the soil surface.

Most crop seeds have specific optimum depths of sowing. This optimum depth varies with seed size, moisture tension, temperature, and soil type. Generally, as seeding depth is increased, large seeds have distinct advantage over small seeds in establishing stand (Black, 1956), but seed emergence is not totally governed by seed weight or seed size (Noda, 1971). Burleigh, Allan and Vogel (1965) reported that at a given planting depths of winter wheat (Triticum aestivum L.) percentage total emergence was lower at 10 C than at 32 C. Parker and Taylor (1965) reported that soil moisture tension and soil type also affected the emergence of sorghum at a given depth. In sandy soil emergence was possible with seeds planted at a greater depth than in clay soil. Within a given soil, increased soil water contents greater than field capacity generally reduced the number of viable seeds planted at any depth due to poor aeration.

The effect of temperature on germination of rice was studied by Chaudhary and Ghildyal (1969). They found a temperature range of 26.5 to 37.5 C was favorable for germination of rice seeds. No germination was observed at temperatures below 4.5 C or higher than 45 C. Alternating temperatures showed no advantage over the constant temperatures for the germination of rice.

Rice varieties, however, differ in the temperatures within which their seeds germinate rapidly and vigorously. The optimum temperature for IRS, IR20 and IR8, for instance, ranged from 19 to 33 C; for IR20 and FUjisaka 5 (a temperate variety from Japan) from 26 to 33 C and for Kulu from 19 to 40 C (International Rice Research Institute, 1971).

In directseeded, flooded rice water depth has a great bearing on the emergence of rice seedlings. Optimum water depth of most rice varieties was found to lie between 5 to 15 em depending on the quality of water (International Rice Research Institute, 1965). The ability of rice seedlings to emerge through 15 em of water was due to their ability to obtain oxygen from the seed through the fermentation process and to germinate with a lower supply of oxygen than other cereal seeds (Taylor, 1942).

The objectives of the following studies were to: (a) Evaluate the effects of seeding depth, soil water contents, pelleting materials, temperature and herbicides on germination, seedling growth or both, and their implications on the effectiveness of pelleted seed, (b) Explore a better way of sowing rice seed on non-flooded, puddled soil for obtaining high percentage of total emergence independent of rainfall or early flooding.

MATERIALS AND METHOD

Seeds were classified as having germinated when the radicle had emerged. Percentage of total emergence was based on the number of rice seedlings emerged from the soil surface.

The germination of rice seed is fairly uniform provided they have been previously soaked in water for 24 hr and are then incubated at 28 C. In this study rice was normally soaked for 24 hr in 1% mancozeb or Dithane M-45 solution (zinc and manganese ethelene bisdithiocarbamate), an effective fungicide against a wide spectrum of plant pathogens. Unless otherwise specified, seedling tests were carried out in petri dishes (100 mm by 15 mm) containing 5 ml of water. The test lasted for 5 to 6 days. The seedlings were grown in the dark at 28 C.

If the objective of the experiment was to study the effect of ^a treatment on the growth of rice seedlings only, the rice seed was first pregerminated by 24 hr soaking and 36 hr incubation. Only seeds with uniform radicle length were selected so as to minimize experimental errors.

All the treatments were replicated three times, and rice variety IR8 was used throughout the experiments. Although each experiment will be discussed separately, there was a strong cause and effect relationship among some of the experiments in that each experiment was conducted as a result of the previous experiment.

Exp. 1. Depth of sowing and water management interaction. The effect of sowing depth and water management on percentage of total emergence of IR8 was studied in the greenhouse using soil obtained from the Paddy-Crop Experiment Station. Fifteen one-gallon cans with holes at the bottoms were filled with upland soil, while another thirty cans without holes were filled with lowland, puddled soils. Presoaked rice seed of variety IR8 was planted at 5 depths; 0, 1, 4, 7 and 10 em. The rate of seeding was 25 seeds per can. The upland soil was kept at field capacity while half of the cans containing lowland soil was kept at saturation point and the other half was flooded with 3 em of water. The date of emergence of coleoptile and the total number of seedling emerged from the soil were recorded. The experiment was terminated 20 days after sowing when no more seedlings were expected to emerge.

Exp. 2. Frequency of irrigation. The poor germination of IR8 seed on puddled, nonflooded soil could be improved by flushing the soil surface with water. However, it is not known how often one should irrigate in order to obtain high percentage of total emergence, and whether or not irrigation can be substituted by burying the seed to a depth of 1 mm . To answer these questions, 36 one-gallon cans were filled with puddled soil. Twenty-five IR8 seeds were sown in each can. The cans were either surface irrigated once, twice, thrice a day,

in two day or in three day intervals. Irrigation was done with a hose by just flushing the soil surface and avoiding flooding. The controlled pots were not irrigated but the seeds were planted at 3 depths: 0, 1 and 10 mm.

The percent total emergence of rice seedlings from each can was recorded 15 days after sowing.

Exp. 3. Soil moisture content. Effect of soil moisture contents on germination, and shoot and root elongation of uncoated and carboncoated rice seed was studied in the laboratory using 15 by 100 mm disposable petri dishes. After soaking, half of the seed was coated with activated carbon Darco G-60 using 50% PVA as an adhesive, while the other half remained uncoated.

Air dry Hauula paddy soil was ground to pass 20 mesh size. Each petri dish was then filled with 50 g of this soil. The moisture contents of this soil were varied from 25 to 60 percent by adding distilled water with a pipette. The water and the soil were mixed gently and thoroughly to avoid spillage. Then 20 rice seeds were sown in four rows on the soil surface. Moisture losses during 6 day incubation at 28 C was prevented by taping the lid firmly on the petri dish with linch masking tape. At the end of incubation, percent germination and length of shoots and roots in each treatment were recorded.

During the same period as the above experiment, the moisture changes of the soil surface and rice seed grown in the greenhouse were studied from sowing time up to 7 DAS. The results of this study were correlated with the findings found in the laboratory in order to determine the critical period in which moisture affects the germination of rice.
Exp. 4. Length of seed pretreatment. Pretreatment of seed before sowing them in the field may be the only practical solution to the poor germination problem in puddled, non-flooded soil. The question is whether use of a pe11eting adsorbent on pregerminated rice seed would inhibit seedling growth. The objective of the experiment was therefore to determine an optimum length of seed treatment prior to coating with activated carbon. Rice seed was soaked and incubated for different lengths of time. After pretreatment, the seed was grown in the germinator for 5 days at 28 C. At the end of this period, the total number of viable seeds, and length of shoot and root were recorded.

The best seed pretreatment found in the above study was applied to the rice seed sown in the greenhouse during the hot, non-rainy days (high temperature 32 C, low temperature 28 C). The percentage of total emergence and plant height of the treated seed was compared to those of presoaked seed at the end of 7 days.

Exp. 5. Removal of co1eopti1e and/or radicle. In a field experiment it was difficult to avoid seed injury during pe11eting of pregerminated seed with activated carbon in a 5-ga11on mixer because the length of radicles and coleoptile varies from 0.2 to 1.5 cm. Severe friction among the seed and between seed and the mixer occurred when more than 1 kg seed was coated at one time, resulting in the breakage of radicle and/or co1eoptile. In the laboratory where only a handful of seed was coated at one time, coating could be done gently in a small beaker. The extent of seed damage during mixing was studied in the laboratory by artificially removing the radicle, the co1eopti1e or both, then growing them in the dark germinator for 6 days after they were coated with activated carbon using 50% PVA as an adhesive.

Exp. 6. Length of seed storage. Another consequence of using pregerminated rice seed in seed pe11eting is the necessity of sowing them in the field as soon as they have been coated, otherwise the seed would dry up and die. In some cases, however, this cannot be done immediately due to bad climatic conditions or untimely land preparation. If such ^a situation arises, the coated pregerminated seed has to be stored until the conditions for sowing are favorable. Twenty-five seeds were sampled for germination counts every day for 6 days to facilitate studying the effect of length of storage on germination. The triple carbon-coated pregerminated rice seed (adhesive: 50% PVA) was kept at 10 C and 25 C.

Exp. 7. Adhesives. In the search for an adhesive which can give a stable coating under flooded and/or heavy rainfall conditions, one of the requirements is the adhesive should not be toxic to rice seed. An adhesive may inhibit germination, seedling growth or both, or it may be inert and nonphytotoxic even at high concentrations. Effect of adhesive on percentage germination and length of shoots and roots was studied by immersing IR8 seed in the adhesive for about 5 minutes. The adhesives were gum arabic, methyl cellulose, methyl ethyl cellulose, dry casein glue and polyvinyl acetate (PVA). After the seed was fully immersed in the adhesives, they were taken out and then dried at room temperature for about three hours. Twenty-five seeds from each batch were placed in the petri dish and then incubated for 6 days.

Exp. 8. Bird repellents. Insecticides and fungicides have been used by some farmers to pellet crop seed to repel birds. Some of these insecticides and fungicides, however, are toxic to seed especially at

high concentrations. Information regarding the use of pesticides in seed pelleting is lacking, and therefore only trial and error can tell us how much insecticide or fungicide is safe for crop seed as well as effective for bird repellent.

Effective concentration for bird repellent may not fall in the range of concentrations found to be safe for seed pelleting. Under these circumstances there must be a way of overcoming toxicity due to the insecticide or fungicide. Diatloff (1970) reported that he could overcome fungicide toxicity to Rhizobia by insulating subterranean clover (Trifolium subterraneum, L.) seed with a polyvinyl acetate layer. This is interesting, since PVA was also found to be the best adhesive in our present study (see Chapter VI). In this experiment the performance of rice seed coated with polyvinyl acetate and then pesticide was compared to that without polyvinyl acetate (the pesticides were dusted on wet seed) and with polyvinyl acetate plus activated carbon Darco G-60. Five pesticides representing a wide range of toxicity to rice seed were used. They are 3% mancozeb (i.e. 3 g material for every 100 g rice seed), 3% methiocarb (4-methylthio-3, S-xylyl-Nmethylcarbamate), 3% carbaryl (l-Naphtyl N-methylcarbamate), 3% dinocap (2-(1-methyl-n-heptyl)-4, 6-dinitrophenyl crotonate) and 1% Dexon (p-(dimethylamino) benzenediazo sodium sulfonate). All the pesticides were in the form of wettable powder.

Exp. 9. Temperature and daylength. Although rice can be grown all year round on Kauai, the rate of growth is much slower in winter than in summer due to low temperature and solar radiation. The extent of reduction of growth rate due to temperature and daylength was determined in this study. The pregerminated seed was grown in the

growth chamber where daylength and night and day temperature could be regulated to approach the conditions found in summer and winter. The temperature treatments were constant temperature of 21 and 28 C and alternating temperatures of 24/18 and 32/24 C. Daylength treatments were 0, 10 and 14 hours.

Exp. 10. Herbicides. The objectives of this experiment were (a) to determine the concentration of herbicides solutions added to give 50% inhibition of the rice plant and (b) to illustrate the effects of herbicides on the length of shoot and roots. Pregerminated rice seed was sown in disposable petri dishes $(100 \text{ by } 15 \text{ mm})$ containing 125 g silica sand and different concentrations of amiben, CP 53619, RP 17623 and 2,4-D IPE. The rice was incubated for five days at 25 C. The detailed procedure of this bio-assay is described in Chapter IX.

RESULTS AND DISCUSSION

Experiment 1

Both water management and sowing depth had highly significant effect on percent total emergence of rice seedlings (Table 7). The interaction between water management and sowing depth was also highly significant. The highest percentage of emergence was obtained at depths of 1 and 4 cm in upland soil. Seedling emergence was very poor at 0 em (surface sowing) and at greater depths; the former was due to frequent drying of the soil surface and the latter was probably due to poor aeration. Only 25% of the seed emerged from the soil at depth of 7 cm. At 10 cm rice seed germinated and grew up to 8 cm high, but after 20 days none of them were able to emerge.

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TABLE 7.. PERCENT TOTAL EMERGENCE OF RICE SEEDLINGS UNDER DIFFERENT SOWING DEPTHS AND WATER MANAGEMENT

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The situation in puddled, non-flooded soil was even worse. Poor emergence occurred at all depths of sowing. When sown on the soil surface, only 36% of the seed emerged. At 1 cm 12% of the seed emerged through cracks in the soil. None of the seeds emerged from greater depths possibly due to poor aeration. The poor aeration of subsoil was intensified when the soil was flooded, as can be seen by the failure of rice seedlings to emerge from a dpeth of 1 cm or greater in the third water management treatment. However, surface sowing produced the highest percent total emergence (84%) compared to the other two treatments, although the growth of seedlings was very slow. Jones (1926 and 1933) also obtained similar results and attributed the poor germination of rice seed covered with soil and a layer of water to an insufficient supply of oxygen.

Experiment 2

Emergence increased as rice seed was more frequently irrigated (Table 8). It appeared that the low percent of rice seedlings emerging from seeds broadcast on the surface of puddled, non-flooded soil was primarily due to lack of moisture, although the soil was initially fully saturated with water at sowing. Irrigating the seed every two days was adequate to get a high percentage of total emergence. Irrigating rice seed every three days improved seedling emergence by 100 percent compared to the control which received no irrigation. Among the control treatments there was a significant improvement in percent total emergence (68%) when rice seed was pushed slightly into the soil instead of sitting on the soil surface. However, if the seed was pushed below the surface (10 mm) only 12 percent emerged from the soil.

 $\sim 10^{-10}$

TABLE 8. PERCENT TOTAL EMERGENCE OF RICE SEEDLINGS ON PUDDLED, NON-FLOODED SOIL UNDER VARIOUS FREQUENCIES OF IRRIGATION

Experiment 3

Increased soil moisture content significantly increased the percent germination and length of shoots and roots in both uncoated and carboncoated rice seed (Figure 4). Germination, however, levelled off at 32.5 percent while length of roots and shoots at about 45 percent. The point where length of shoots and roots started to level off coincided with soil field capacity, which was 47.6 percent.

Permanent wilting point as determined by bioassay in the greenhouse was 25.9 percent. At this moisture content rice seed was unable to germinate. At a moisture content of 27.5 percent only 23 percent (uncoated seed) to 46 percent (coated seed) germinated but the germinated seed were imperfect and only the radicles were developed. Coleoptile growth began at 30 percent moisture in both coated and uncoated seed.

The magnitude of root and shoot growth was significantly greater with carbon-coated seed than uncoated seed at moisture contents greater than 35 percent, although both seeds were incubated at the same temperature for the same period of incubation. Large increases in shoot and root growth of carbon-coated seed could be due to the ability of black carbon to absorb heat and to adsorb whatever toxic products were present in the soil.

Changes in moisture contents of rice seed and surface soil during the first week of braodcasting seed on puddled, non-flooded soil in the greenhouse are presented in Table 9. These data indicate that during the first three days after sowing there was not very much change in moisture contents of rice seed or soil surface. The moisture content

FIGURE **4.** PERCENTAGE OF GERMINATION AND LENGTH OF SHOOT AND ROOT OF UNCOATED AND CARBON-COATED RICE AT DIFFERENT SOIL MOISTURE CONTENTS

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TABLE 9. CHANGES IN MOISTURE CONTENTS OF RICE SEED AND SURFACE SOIL DURING THE FIRST WEEK OF BROADCASTING RICE SEED ON PUDDLED, NON-FLOODED HAUUIA PADDY SOIL

of the soil began to drop from 155 percent to 122 percent on the fourth day and finally to 83 percent on the eighth day. Moisture content of rice seed dropped from 49.7 to 39.2 on the fourth day and remained stable at about 38 percent until 7 DAS. The moisture content of rice seed might be overestimated, since there was difficulty in separating seed from mud present on the surface of the seed, even with vigorous rubbing.

The fact that moisture content of the surface soil was still high on the eighth day, almost twice as high as the soil field capacity, suggests that soil moisture alone was not responsible for the low germination of rice seed broadcast on the soil surface. As the water on the soil surface evaporated and the soil hardened and started to crack on the fourth day there might have been a rapid decrease in the rate of diffusion of water to the seed. Probably water diffusion was not fast enough to compensate for water losses from the seed as a result of direct exposure of seed to sunlight. The rapid losses of water from the seed at this stage was probably responsible for the failure of the seed to emerge from the soil, since radicle formation had just started.

Experiment 4

The longer rice seed was incubated the sooner the radic1es emerged from the coated seed (Table 10). The emergence of radicles from carboncoated seed was generally one day late compared to uncoated seed. Soaking seed did not have much effect in hastening radicle emergence, but soaking plus incubation up to 36 hours reduced the waiting period from three to one day. This was significant since puddled soil was

TABLE 10. EFFECT OF VARIOUS SEED PRETREATMENTS ON GERMINATION AND GROWTH OF CARBON-COATED AND UNCOATED RICE SEED

UNCOATED RICE SEED

 $*DAS = days after solving$

 ~ 100 km s $^{-1}$

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 $\sim 10^7$

fully saturated with water during the first three days. Once coated seed emerged on the second day, they were able to survive the lack of water on the fourth day, since their roots would have been well developed by this time.

Incubation longer than 36 hours significantly reduced the length of shoots and roots of coated seed compared to other treatments, possibly due to the injury of the seed during pelleting. The length of the radicles of seed incubated for 48 hr was about 15 mm, compared to only about 0.5 mm for seed incubated for 36 hr. The longer the radicles, the more difficult it was to avoid breakage of radicles and/or coleoptile during pelleting.

The best seed pretreatment appeared to be 24 hr soaking plus 36 hr incubation. In practice, incubation is carried out by covering presoaked rice seed with layers of wet burlap sacks. The burlap sacks keep the seed moist at a higher temperature which permits more uniform and rapid germination.

The best seed treatment obtained above was used in the greenhouse to see whether percentage of total emergence could be improved in this way. Data presented in Table 11 clearly demonstrate the advantages of presoaked plus preincubated rice seed over presoaked seed in terms of percent total emergence and plant height. The percent total emergence of the former treatment was three times higher than the latter: 95 percent vs. 31 percent. The difference in percent total emergence between coated and non-coated seed was not significant. A week after sowing the seedlings from presoaked and preincubated seed reached a height of 96 mm while those from presoaked seed that survived was only 32 mm tall.

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TABLE 11. EFFECT OF TWO SEED PRETREATMENTS ON PERCENT TOTAL EMERGENCE AND HEIGHT OF BOTH COATED AND UNCOATED RICE SEEDS SOWN ON PUDDLED, NON-FLOODED SOIL

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A high percentage of emergence coupled with rapid increase in plant height are the primary goals sought for to obtain high seedling survival of coated seed from toxic chemicals. Rapid increase in plant height will allow early flooding before the soil begins to crack seriously as a result of intense drying during hot days. All these advantages were possible without irrigating the soil for seven days or pushing the seed into the soil.

Experiment 5

Partial or complete removal of radicles from the rice seed during seed pelleting did not reduce either percent seedling survival nor shoot growth (Table 12). However, their roots were significantly shorter than those of the control. Removal of coleoptile or both coleoptile and radicle from rice seed significantly decreased seedling survival and rate of growth of both shoots and roots. These data suggest that injury of the coleoptile and not the radicle was responsible for the reduced seedling survival of coated seed observed both in the laboratory and in the field. This reduction was about 15 percent in the field compared to seed which was not pelleted.

Experiment 6

There was no apparent reduction in percent germination when the coated, pregerminated rice seed was stored for up to 5 days at 10 C or 25 C (Table 13). At room temperature (25 C) there was 10 percent decrease in percent germination after 6 days storage but the surviving seedlings still looked healthy during incubation.

When dealing with a bulk quantity of coated seed (more than 1 kg) it was found better to store them at $10 - 15$ C to prevent the sprouting

TABLE 12. EFFECT OF REMOVAL OF RADICLE AND/OR COLEOPTILE ON SEEDLING SURVIVAL AND GROWTH OF PREGERMINATED, COATED RICE SEED

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TABLE 13. EFFECT OF LENGTH OF STORAGE ON PERCENTAGE OF GERMINATION OF CARBON-COATED, PREGERMINATED RICE SEED

of radic1es. At 25 C, about 10 percent of the seed sprouted after a few days because temperature inside the bag was higher than outside the bag. Sprouted, coated seed were found to be easily killed by herbicide as soon as they were sown in the soil.

Experiment 7

Dry casein glue was very toxic to rice seed while the other adhesives had no effect on germination and seedling growth (Table 14). About 64 percent of rice seed did not germinate when 20% dry casein glue was coated around them. The remaining seed survived but with markedly reduced growth of roots and shoots. The toxicity of dry casein glue can probably be attributed to the extremely high pH of the adhesive solution. The pH of 20% dry casein glue was 12.3, while the pH of the other adhesive ranged from 4.1 to 8.3 (Table 18).

Experiment 8

Mancozeb, methiocarb, carbaryl, dinocap and dexon had varying effects on rice seedlings when they were dusted on rice seed. Mancozeb improved seedling growth, methiocarb was slightly toxic while the rest were highly toxic to rice seed (Table 15). The germination might be high, but the seedlings were imperfect as in the case of seed treated with carbaryl and dexon.

Insulating rice seed with a polyvinyl acetate layer before dusting the pesticides did not reduce their toxicity to rice seed. In fact, the growth of such seed was worse than the previous treatment possibly because more of the pesticides were coated around the seed.

Coating of rice seed with polyvinyl acetate and pesticide followed immediately by activated carbon Darco G-60 significantly improved

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 $\alpha = 1$, where the continuous continuous continuous continuous continuous continuous $\{x_0, \ldots, x_n\}$

TABLE 14. EFFECT OF SOME ADHESIVES ON PERCENT GERMINATION AND GROWTH OF RICE SEED

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TABLE 15. THE ROLES OF POLYVINYL ACETATE (PVA) AND ACTIVATED CARBON IN REDUCING TOXICITY OF INSECTICIDES AND FUNGICIDES USED AS SEED PELLETING MATERIALS

LSD (0.05)

Germination 7

Shoot 8

Root 12

...
...

percent germination as well as seedling growth. None of the seed showed any sign of toxicity. The explanation for this phenomenon is quite simple. Activated carbon has tremendous adsorption capacity toward organic substances (Hassler, 1963). Most of the pesticides applied were probably all adsorbed by the carbon before they could cause any injury to the seed. This coating technique was applied in the bird repellent study because pesticide losses in flooded water were also totally prevented by the carbon layers (see Chapter VII).

Experiment 9

Growth rate of rice seedlings was not significantly affected by increasing daylength from 10 to 14 hours, but seedlings grown in the dark showed significantly longer but thinner roots than if they were exposed to alternating light and dark (Table 16). Temperature played a prominent role in rate of elongation of shoot and root under all types of light treatments. Under continuous dark, for every centrigrade decrease in temperature there was 0.43 mm/day reduction in the rate of elongation of both root and shoot. Under alternate light and dark treatments this reduction was 0.65 mm/day.

The shoot/root ratio (by weight) of seedlings grown in the dark was significantly higher than that of the seedlings grown in alternating dark and light, suggesting that under the former conditions most of the food reserves in the seed were used to manufacture shoot, whereas under the latter conditions the food reserves were equally divided for root and shoot growth.

| Temperature (C) Night Day | | Daylength (hr) | Rate of Growth (mm/day) | | Shoot/Root Ratio |
|---------------------------------|----|-------------------|----------------------------|------|---------------------|
| | | | Shoot | Root | |
| 21 | 21 | 0 | 8, 2 | 12.0 | 1.46 |
| 28 | 28 | 0 | 11.2 | 15.0 | 1.46 |
| 24 | 18 | 10 | 5.7 | 6.9 | 1.18 |
| 24 | 18 | 14 | 5.3 | 6.7 | 1.00 |
| 32 | 24 | 10 | 9.3 | 10.2 | 1.12 |
| 32 | 24 | 14 | 9.8 | 11.0 | 1.02 |
| | | LSD (0.05) | 1.4 | 1.5 | 0.11 |

TABLE 16. GROWTH RATE OF PREGERMINATED RICE SEED UNDER DIFFERENT LIGHT AND TEMPERATURE REGIMES

Experiment 10

Figure 5 shows that amiben and 2,4-D reduced root growth more than shoot growth while the reverse was obtained with CP 53619 and RP 17623. Amiben toxicity to rice and other species was characterized by severe inhibition of root development without a corresponding decrease in shoot growth. In upland soil the plants die quickly due to their inability to take up moisture and nutrients, but in flooded soil the injured rice seedlings often floated during the first few weeks after amiben application and then survived and recovered after their roots started to develop in the mud.

Both roots and shoots were inhibited by CP 53619 but I_{50} value (the concentration of herbicide solutions added to give 50 percent inhibition of the test plant) for shoot was slightly lower than for roots.

Rice was highly resistant to RP 17623 but highly sensitive to 2,4-D IPE. The herbicide concentrations at which 50 percent of the inhibition of rice plant (either root or shoot) was obtained were 0.14, 0.77, 3.3 and 128.0 ppm for 2,4-D IPE, amiben, CP 53619 and RP 17623, respectively. The rice seedlings injured by RP 17623 were characterized by brownish discoloration of the oldest leaf as well as the leaf sheath. The symptoms increased with time, and the plants eventually died due to breakage of the stem. The action of RP 17623 was rather slow, being two to three weeks, so that it was actually difficult to evaluate its true I_{50} value in a short experiment like this.

FIGURE 5. EFFECT OF DIFFERENT CONCENTRATIONS OF HERBICIDES ON LENGTII OF SHOOT AND ROOT OF RICE

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 $\sim 10^{-1}$

SUMMARY AND CONCLUSIONS

The poor germination of rice seed on puddled, non-flooded soil was attributed to its inability to utilize soil moisture when it was still abundant on the soil surface during the first three days after sowing. It took three to four days for presoaked rice seed to germinate. By the time it finally germinated the surface soil was already hard and dry. This germination problem could be overcome by pushing the seed to a depth of 1 mm or by irrigating them every day or every other day, but these methods are considered impractical.

Pregerminating rice seed before they are sown were shown to be the only practical solution to the poor germination on non-flooded soil. Not only the percent total emergence was high, but also the seedlings could grow three times as fast as the conventional presoaked seed.

Seed pelleting carried out with pregerminated seed did not cause any injury, provided the radicles were still small. Optimum incubation at 28 C was found to be 36 hr. The coated, pregerminated seed could also be stored for at least 6 days at 10 C or 25 C in the shade without causing any significant reduction in percentage of germination.

Of the five adhesives studied only dry casein glue was found to be toxic to rice seed. Polyvinyl acetate was not toxic but played no role in reducing the toxicity of insecticides and fungicides to rice seed as claimed by Diatloff (1970). The toxicity of these pesticides could be neutralized by coating them with both activated carbon and 50% polyvinyl acetate.

Low temperatures reduced seedling growth by 27 percent in the dark and 42 percent under alternating dark and light.

Amiben and 2,4-D IPE reduced root growth of rice more than that of the shoot. The reverse was obtained with CP 53619 and RP 17623. The two former herbicides were highly toxic while the latter were moderately toxic to rice seed. This implies that adsorbent-coated seed would have less chance to survive from amiben and 2,4-D IPE than from CP 53619 and RP 17623 because small quantities of the herbicides remaining in the soil are still detrimental to rice seedlings.

CHAPTER VI. DEVELOPMENT OF PELLETING MATERIALS AND TECHNIQUE

In an attempt to find the best pelleting materials, ideally one should screen all the adhesives and adsorbents which are commercially available. However, with limited time, money and facilities this approach would be too complicated and laborious. Furthermore, since our second objective was to develop a pelleting technique that would most likely succeed in the field, it was considered better to limit the number of adhesives and adsorbents to a number that could be tackled. The best pelleting materials found in the study were then tested further in the greenhouse and in the field with different herbicides, soils, methods of application, climatic conditions and other factors in order to evaluate their potentials and limitations.

The objectives of this study were to:

a. Find an adhesive which is not toxic to rice seed, easy to handle and gives a stable coating under adverse climatic conditions.

b. Find an adsorbent or a combination of adsorbents that will provide the most protection to directseeded rice from toxic herbicides.

MATERIALS AND METHODS

Laboratory Experiments

Plucknett (1971) reported that aqueous solutions of 45% gum arabic, 5% methyl cellulose and 4% methyl ethyl cellulose have been used successfully in seed pelleting work in New Zealand and Australia. Seaman and Brandon (1971) reported that 50% polyvinyl acetate and 20% dry casein glue were also potentially good adhesives for pelleting rice seed.

The above five adhesives were selected in order to compare their coating quality and stability by varying their concentrations and coating layers of adsorbents.

The main adsorbent used for evaluating coating quality and stability was activated carbon Darco G-60. This adsorbent had the highest efficiency in adsorbing herbicides compared to Darco 5-51, Darco KB, Darco M and Darco-B (Coffey and Warren, 1969). Two other adsorbents anion and cation exchange resins **--** were selected for this study. Their chemical and physical properties are presented in Table 17.

The pH and viscocity of the adhesives were determined for each concentration used.

Coating quality was judged visually by observing if the carbon could cover the entire surface of slender rice seed. Perfect coating should cover the entire surface of rice seed with easy separation of the surplus adsorbent from the coated seed. Pelleting quality was arbitrarily classifed as excellent, good, fair and poor.

Pelleting or coating stability was found to be best evaluated by shaking 20 coated seed in a vial containing 20 ml of water for at least 2 minutes (the shaking time was standardized to 2 minutes). The seed was shaken on a Burrell wrist-action shaker. After shaking, the coated seed was placed on a dry paper for visual determination of coating stability. A score of 10 was given to the coating which remained intact after shaking and a score of 0 to coatings which completely dispersed in water. This stability test proved to be better and more practical than other methods such as subjecting coated seed with a given amount of simulated rainfall, or by placing the

TABLE 17. PROPERTIES OF ACTIVATED CARBON AND EXCHANGE RESINS

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seed on wet filter paper and noticing the movement of adsorbent away from the seed with time.

Percent germination and length of shoot and root were used to evaluate the toxicity of adhesives to rice seed.

Weight of adsorbent for seed was determined by a difference between weight of 100 coated seed and 100 uncoated seed.

Thus, weight of adsorbent/seed =

weight of 100 coated seed - weight of 100 uncoated seed 100

After several preliminary trials, the pelleting method in the laboratory was standardized by adding 5 ml adhesive and 5 g adsorbent to every 10 g of rice seed. Since exchange resins came as wet beads, not as wettable powder, they had to be pretreated before they could be used. Pretreatment of both cation and anion exchange resins consisted of several washings with water and alcohol on large buchner funnels, oven drying of the washed samples and then grinding them to pass 100 - 200 mesh size.

Seed pelleting was carried out in a small beaker. First the adhesive was mixed with the seed thoroughly with a glass rod. After thorough wetting of the seed, the adsorbent was added to coat the seed as well as to separate lumps of seed. Normally, lumps of seed will not form unless excess adhesive is added. Uniform coating was made by stirring the wet seed and adsorbent with a glass rod for a few minutes.

The weight of the adsorbent can be increased by increasing the number of coating layers on the seed. In this study the number of coatings was limited to three since beyond this number, it became impractical and costly. The number of coating layers was increased by repeating the above pe11eting procedure after the seeds were dried for at least 60 minutes. In some cases, slightly more adhesive was needed for the second and third coatings.

The cation exchange resin presented ^a special problem when it was used for seed pe11eting. The adsorbent tended to form large granules as soon as it was added to wetted rice seed. Consequently, the resulting coating on the seed was very poor and irregular in shape. Furthermore, the rice seed was not easily separated from the surplus adsorbent after pe1leting was completed. The coating quality of cation exchange resin was improved by mixing it with activated carbon in a ratio of 1 to 2 prior to coating.

Greenhouse Experiments

The efficiency of the three adsorbents in protecting rice seed from amiben, CP 53619 and RP 17623 was evaluated by pel1eting them on rice seed singly or in combination. The adsorbents were combined in two ways:

a. by pel1eting rice seed with one adsorbent followed by another adsorbent.

b. by mixing two or three of the adsorbents together before they were pe11eted around the seed. The ratio of the adsorbents in the mixture was either 2 parts of carbon for every part of exchange resin or 3 parts of carbon $+$ 2 parts of anion exchange resin $+$ one part of cation exchange resin.

The seeds were coated with adsorbents using 50% polyvinyl acetate as an adhesive.

The coated, pregerminated rice seed was sown in yellow plastic pots. The pot inside dimension was 27 and 30 cm, and the depth was 12 em. Such a pot could accommodate 6 rows of rice seed with 10 seeds per row. Each row represented one coating type. The herbicides were sprayed uniformly on the puddled soil just after the seed was sown. The rates of application were 2.24, 1.65 and 3.36 kg/ha for amiben, CP 53619 and RP 17623, respectively.

Each treatment was replicated three times. Seedling survival was determined two weeks after sowing. Plant heights were taken 14 DAS and again when the crop was harvested 5 to 6 weeks after sowing. The average number of tiller per hill was computed by dividing the total number of tillers by the number of seed surviving in each pot.

RESULTS AND DISCUSSION

Laboratory Experiments

The coating quality and stability of methyl cellulose, methyl ethyl cellulose, gum arabic, dry casein glue and polyvinyl acetate at different concentrations are presented in Table 18. In general, increasing the concentrations of the adhesives increased the quality and the weight of carbon coatings. The shape of rice seed was such that it was very difficult to coat the entire seed if the concentration of the adhesive was not right. However, with methyl cellulose and methyl ethyl cellulose, increased concentrations were accompanied by increased viscocity. Highly viscous adhesive solutions were undesirable because of the difficulty in coating seed with adsorbents. On the basis of coating quality alone the optimum concentrations of the adhesives were 2, 7.5, 45, 20 and 50 percent for methyl cellulose,

TABLE 18. PROPERTIES OF SOME ADHESIVE AS MATERIALS FOR COATING RICE SEED WITH ACTIVATED CARBON DARCO G-60

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TABLE 18. (CONTINUED) PROPERTIES OF SOME ADHESIVE AS NATERIALS FOR COATING RICE SEED WITH ACTIVATED CARBON DARCO G-60

*Coating stability score: $10 = \text{most stable}$, $0 = \text{least stable}$

methyl ethyl cellulose, gum arabic, dry casein glue and polyvinyl acetate, respectively.

The coating stability of the five adhesives was strikingly different. Coatings made from gum arabic was highly unstable. In fact, their coatings easily dispersed as soon as the coated seed touched the water. The coating stability of both methyl cellulose and methyl ethyl cellulose was fair but the most stable coatings were made from dry casein glue or polyvinyl acetate. Coating stability was generally not affected by the concentrations of the adhesives.

Between dry casein glue and polyvinyl acetate, the choice was determined by their effect on germination and seedling growth. As discussed earlier (Chapter V) dry casein glue used alone was highly toxic to rice seed. Dry casein glue used in combination with activated carbon was not very toxic but the percentage of germination was :;ignificant1y lower than that of polyvinyl acetate. It can be concluded that among the five adhesives, polyvinyl acetate was the best adhesive for seed pelleting.

In Table 19 the number of activated carbon coating was varied from one to three using optimum concentrations of methyl ethyl cellulose, gum arabic, dry casein glue and polyvinyl acetate. Although increasing the number of coatings from one to three did not improve their stability, the weight of activated carbon per seed was significantly increased by about three fold. It was also observed that the more dry casein glue was used for seed pel1eting, the more toxic it was to rice seed. The coatings made from 50% polyvinyl acetate are shown in Plate 2.

TABLE 19. EFFECT OF NUMBER OF COATING LAYERS OF CARBON ON WEIGHT AND STABILITY OF COATING

*Stability score: $10 = \text{most stable}$, $0 = \text{least stable}$

PIATE 2. THE INCREASE IN SEED SIZE AND COATING WEIGHT AS RICE SEED WAS COATED WITH ACTIVATED CARBON FROM ONE TO THREE TIMES.

PIATE 3. COATING QUALITIES OF RICE SEED COATED WITH ANION EXCHANGE RESIN, CATION EXCHANGE RESIN, ACTIVATED CARBON AND A COMBINATION OF THE THREE ADSORBENTS.

There was no doubt that coatings made from polyvinyl acetate were extremely stable. These coatings did not easily disperse in water as indicated by low amounts of activated carbon (2-4 percent) dispersed in water after they were shaken for 60 minutes.

The nature and properties of adsorbents also determined coating quality (Table 20). The cation exchange resin coating was poor even though 50% polyvinyl acetate was used as an adhesive (Plate 3). This was due to the tendency of the cation resin to form granules as soon as it came into contact with water. Anion exchange resin coating was good although the coating layer was very thin compared to activated carbon. Combining the exchange resins with activated carbon prior to coating them with seed improved the coating quality but not the coating stability.

Cation exchange resin was also slightly toxic to rice seed compared to other adsorbents.

Greenhouse Experiments

The performances of activated carbon, anion exchange resin and cation exchange resin used alone were compared to those of uncoated seed, triple carbon-coated seed and a combination of the three adsorbents. The results are presented in Table 21 and Figure 6.

The increasing order of phytotoxicity of herbicides to both coated and uncoated seeds were CP 53619, RP 17623 and amiben. Seedlings injured by CP 53619 recovered quickly within 14 days. At 30 days after sowing the surviving seedlings recovered completely, as shown by lack of significant differences in plant height and tiller number per hill of coated and uncoated seed. RP 17623 was moderately toxic to plants

·TABLE 20. COATING QUALITY OF 3 ADSORBENTS USED SINGLY OR IN COMBINATION USING 50% POLYVINYL ACETATE AS AN ADHESIVE

*Stability score: $10 = \text{most stable}$, $0 = \text{stable}$ **fb. = followed by

TABLE 21. EFFECT OF AMIBEN, CP 53619 AND RP 17623 ON SEEDLING SURVIVAL, HEIGHT AND TILLER NUMBER OF RICE SEED COATED WITH THREE ADSORBENTS

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 $*fb$. = followed by

 $\sim 10^{-11}$

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FIGURE 6. EFFECT OF AMIBEN, CP 53619 AND RP 17623 ON FRESH WEIGHTS OF RICE COATED WITH THREE TYPES OF ADSORBENTS

 $\sim 10^{11}$ km s $^{-1}$

from both coated and uncoated seed. Both shoot and root growth were only moderately inhibited. Brown lesions were observed on leaves as well as leaf sheaths. At harvest (6 weeks after sowing) the injured seedling still showed some degree of stunting although tiller development was not inhibited.

Amiben was highly toxic to both coated and uncoated seed even at 2.24 kg/ha. The injured seedlings showed pronounced root inhibition, and the seedlings appeared pale green and stunted and the leaves showed onion-leaf symptom similar to 2,4-D. Tillering was also inhibited. Highly injured seedlings generally floated once water was introduced since their roots did not anchor firmly in soil. The floating seedlings usually recovered if they were not too severely injured.

The performance of the adsorbent-coated seed closely followed with the degree of toxicity of the herbicides. The percentage of seedling survival of uncoated seed ranged from 23 to 30 percent under the three herbicide treatments (Table 21). Its fresh weights were less than 10 percent of the controlled plots (Figure 6). The anion exchange resin and cation exchange resin coatings only slightly improved the percentage of seedling survival and fresh weights of rice in all the herbicide treatments. The single carbon-coated rice seed, however, performed significantly better than the uncoated rice under the three herbicide treatments, especially CP 53619. Their performance was in fact equal or better than rice seed coated with the three adsorbents. The best coating treatment, however, was those seed which were coated with activated carbon three times. Triple carbon-coated rice seeds

had high seedling survival even under amiben treatment. Plants showed some toxicity at the early seedling stage, but they quickly recovered about a month after sowing.

The excellent performance of triple carbon-coated rice seed was again obtained in the second greenhouse experiment where it was compared to rice seed coated with single layer of carbon and a single layer of a mixture of two or three adsorbents including activated carbon and exchange resins. The latter coated seeds showed some degree of toxicity from CP 53619 and RP 17623, but their fresh weights at 5 weeks after sowing were not significantly different from the control (Table 22 and Figure 7). However, under amiben treatment they performed very poorly. The triple carbon-coated rice seed, on the other hand, showed negligible toxicity, and its fresh weights were comparable to that of the control treatment under the three herbicide treatments (Figure 7).

These results suggest that both coating quality and quantity were important in overcoming herbicide toxicity in directseeded rice. One of the causes of the failure of exchange resins to perform as well as activated carbon was probably due to their poor coating quality. The failure of single carbon-coated seed to perform as well as triple carbon-coated seed was probably due to the insufficient amount of adsorbent to neutralize the herbicide toxicity around the seed. The activated carbon and exchange resin mixtures would probably have done well too, if they were coated two to three times but this was not done because of cost. Exchange resins were five times more expensive than activated carbon.

TABLE 22. EFFECT OF AMIBEN, CP 53619 AND RP 17623 ON SEEDLING SURVIVAL, HEIGHT AND TILLER NUMBER OF RICE SEED COATED WITH DIFFERENT ADSORBENT COMBINATIONS

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FIGURE 7. EFFECT OF AMIBEN, CP 53619 AND RP 17623 ON DRY MATTER OF RICE COATED WITH SEVEBAL ADSORBENT CCMBINATIONS

הוא המונים לאחרים של המשמע לאחרים את המונים האופן את המונים ביותר ביותר ביותר ביותר ביותר את המונים של המונים ש
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 \sim

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DRY MATTER (gm/pot)

医阴道 医血管膜炎 医无子宫

SUMMARY AND CONCLUSIONS

The pe11eting properties of five adhesives (methyl cellulose, methyl ethyl cellulose, gum arabic, dry casein glue and polyvinyl acetate) were studied by varying their concentrations and the type and the nmnber of layers of adsorbents. Pe11eting quality was improved by increasing the concentration of the adhesives, but increased concentrations were often accompanied by increased viscocity of the adhesive solutions which were undesirable in seed pelleting. Optimum concentrations of methyl cellulose, methyl ethyl cellulose, gum arabic, dry casein glue and polyvinyl acetate were 2, 7.5, 45, 20 and 50 percent, respectively. Of these adhesives, dry casein glue and polyvinyl acetate gave the most stable coatings when activated carbon was used as an adsorbent. But polyvinyl acetate was selected in the subsequent experiments because dry casein glue was toxic to rice seed.

Coating stability was also affected by the nature of the adsorbents but not the nmnber of coating layers. Cation exchange resin gave poor and unstable coating compared to activated carbon and anion exchange resin because of its tendency to form granules upon contact with water. Anion exchange resin coating was excellent although the coating layer was relatively thin.

Of the three adsorbents studied, activated carbon gave the best protection to rice seed from amiben, CP ⁵³⁶¹⁹ and RP ¹⁷⁶²³ when it was coated three times. Anion and cation exchange resins used alone or in combination with activated carbon were inferior to triple layers of activated carbon.

The degree of protection appeared to be proportional to the weight of adsorbent coated around the rice seed, although coating

quality might also be important. A single layer of activated carbon was adequate to protect rice seed from CP 53619 but not to highly toxic RP 17623 and amiben.

It is concluded that triple layers of activated carbon Darco *G-60* and 50% polyvinyl acetate were the best pelleting materials found thus far. This adhesive + adsorbent combination was tested further in both the greenhouse and the field under different conditions.

CHAPTER VII. FACTORS AFFECTING THE PERFORMANCE OF TRIPLE CARBON-COATED RICE SEED IN FLOODED SOIL

In the earlier greenhouse experiments (Chapter VI) it was found that activated carbon Darco *G-60* used alone was better or comparable to either exchange resins or combinations of exchange resins and activated carbon. Increasing the number of carbon layers to three, in fact, tremendously improved the performance of coated seed in soil treated with amiben, CP 53619 and RP 17623.

The performance of triple carbon-coated rice seed was tested further in these studies under different sets of conditions in the greenhouse and the field to:

a. Determine whether improvements could be made by manipulating time of flooding, time of herbicide application, seeding rates, and types of activated carbon.

b. Define factors that limit the effectiveness of carbon-coated seed.

c. Evaluate climatic and soil effects on the performance of carbon-coated seed.

MATERIALS AND METHODS

Pot Experiments

General. A series of pot experiments were conducted from February 1971 until May 1972 at the Hawaii Agriculture Experiment Station on Kauai. The procedures of these experiments were basically the same so that general description of the procedure was given here in order to avoid repetition.

Plastic pots measuring 27 and 30 cm and a depth of 13 cm were filled with 9 kg of puddled soil from Wailua valley. After the soil was fertilized with ammonium phosphate, it was levelled and excess water was drained out of the pots. Rice seeds (Oryza sativa, var. IR8) were first pregerminated by soaking them in water for 24 hr and then incubating them at 28 C for 36 hr. Half of the pregerminated seed was coated with activated carbon Darco G-60 three times using 50% polyvinyl acetate, and the other half remained uncoated, except for experiment No.9. The resulting coating weight varied from 13 to 17 mg per seed. Unless otherwise specified, both coated and uncoated seeds were sown in the same pot. This was done by planting three rows of uncoated seed in one end, and three rows of coated seed in another end. Each row consisted of 10 seeds spaced 2.5 em apart. The distance between rows was 4 em. Each pot received the same herbicide treatments. This was a split plot design. The design was utilized intensively here in order to cut down the number of pots to as few as possible due to a lack of space in the greenhouse. The main plot treatments were herbicides alone or a factorial combination of herbicides with other treatments, such as time of flooding or methods of herbicide application.

When it was necessary to assess the effect of herbicides on both rice seed and weeds, barnyardgrass seed was broadcast and incorporated in the soil before sowing rice seed.

Unless specified otherwise, herbicides were applied shortly after the rice was sown. The three main herbicides used were amiben, CP 53619 and RP 17623. They were usually applied at the rates of 2.24, 1.65 and 3.36 kg/ha, respectively. Other herbicides were also used but these will be mentioned later.

Rice was grown for about five weeks before fresh weights or dry weights were obtained from each treatment. Seedling survival was counted two weeks after sowing/herbicide application and again at harvest time.

The number of replications was kept to three, except in pot experiment No. 9 where each treatment was replicated four times.

Exp. 1. Time of flooding. Time of flooding was shown to be very critical to the survival of carbon-coated rice seed (Chapter IV). To determine the best time to flood the soil, an experiment was conducted whereby treated pots were flooded at different times, starting from two days after sowing (when the radic1es had just emerged) up to 11 days after sowing (corresponding to 2 to 3 leaf-stage of rice seedlings). The depth of water initially kept at 2 to 3 em for about two weeks. Thereafter, the water level was increased to 5 to 7 em. The growth of seedlings in these pots was compared to seedlings grown in pots which did not receive herbicide treatments.

Exp. 2. Rates of herbicide application. The effect of different rates of amiben, CP 53619 and RP 17623 on the growth of carbon-coated seed was evaluated by varying the rates of application from 1.12 kg/ha to 4.48 kg/ha with 1.12 kg/ha increments. The objective was to determine the dependence of the performance of carbon-coated rice seed on rates of application.

Exp. 3. Time of herbicide application. Amiben, CP 53619 and RP 17623 were applied two days before sowing, at sowing and two days after sowing in order to determine whether early application (before sowing) would improve the performance of carbon-coated seed by allowing

the herbicides to equilibrate first with the soil. Also, it was done to determine whether late application was detrimental to carbon-coated seed as a result of lack of time interval between herbicide adsorption by carbon coating and the emergence of radicles and coleoptiles.

Exp. 4. Method of application. Some herbicides must be incorporated into the soil in order to obtain effective weed control and to prevent herbicide losses due to volatilization (Jordan, et al., 1963 and 1968; Linscott and Hagin, 1967; Wiese and Smith, 1970). Herbicides incorporated into soil might not be adsorbed effectively by carbon-coated seeds which are sown on the soil surface. Furthermore, the presence of herbicides in subsoils might be injurious to rice seedlings since such herbicides could be absorded by roots. To study the effect of herbicide incorporation on the performance of carboncoated seed, amiben, CP 53619 and RP 17623 were applied in two ways. In the first treatment, these herbicides were sprayed on the soil surface in the usual manner. But in another treatment, the herbicides were incorporated to a depth of 3 em soon after they had been sprayed on the soil surface.

Exp. 5. Distance of planting. The amount of activated carbon applied to the soil per unit area can be increased by increasing the seeding rates of carbon-coated rice seed. The amount of herbicide which is adsorbed is in direct proportion to the amount of carbon applied (Jordan and Smith, 1971). Thus, the total herbicide per unit area and/or the amount of herbicide present around the coated seed can be reduced by increasing the seeding rates of coated seed. This problem was studied by planting the seed at spacings of 1×1 cm,

2 x 2 cm, 3 x 3 cm and 4 x 4 em, which were equal to seeding rates of 3000, 750, 333 and 187.5 kg/ha, respectively. The pots were treated with 2.24 kg/ha amiben and 3.36 kg/ha CP 53619. Higher rates than 1.65 kg/ha was used, since at 1.65 kg/ha CP 53619 was not very toxic to triple carbon-coated seed. Uncoated seed was not planted at all. Instead, the results were compared to the control which was not treated with herbicide.

Exp. 6. Soils. The performance of triple-carbon-coated rice seed was tested in other lowland (flooded) soils taken from Hanalei and Hanapepe valleys, the principal taro growing areas on Kauai. The Hanalei soil (pH 5.39, O.M. 5.04%, CEC=33.83 meq/100 g and clay 34.5% belongs to the same series as Hauula paddy soil in Wailua valley. The Hanapepe soil (pH 5.02, 0.M. 5.11%, CEC=34.04 meq/100 g and clay 29.4%), however, belongs to Pakala series. The textures of these two soils were classified as clay loam and sandy clay loam, respectively. Since Hanalei and Hanapepe soils contained about the same organic matter contents, it was considered necessary to mix Hanalei and Wailua soils in equal proportions to get a fairly wide range of organic matter contents. The two soils were mixed in a concrete mixer. The resulting soil had the following properties: pH 4.92, O.M. 7.26%, CEC=39.49 meq/100 g and clay 44.4%). The Wailua soil used in this study had the following properties: $pH 4.61$, 0.M. 12.26, CEC=41.83 meq/100 g and clay 54.6%).

Exp. 7. Formulation. In the preliminary field experiment reported in Chapter IV granular herbicides were not effective in controlling weeds when they were applied on nonflooded, puddled soil. Since then

there had been some preliminary trials to determine the best water management to obtain both effective weed control and high percentage of seedling survival of coated seed. This problem could be solved by first applying granular herbicides on flooded soil seven days before sowing; thereafter, the water was drained and the carbon-coated seed was sown on the drained soil. After another seven days the soil was reflooded. This unique water management worked well with granular herbicide combination S-ethyl dipropylthiocarbamate (EPTC) $+$ $((4{\text{-}chloro-o-tolyl)oxy})$ acetic acid (MCPA) at the rate of $(1.75 + 0.7)$ kg/ha. It was then decided to conduct further experiments using other granular herbicides which were found excellent for transplanted rice but were very toxic to directseeded flooded rice (International Rice Research Institute, 1969 and 1970). The herbicides were (2,4-dichlorophenoxy)acetic isopropyl ester (2,4-D IPE); α -2,2,2-trichloroethyl styrene (TCE-styrene); α β -trifluoro-2,6dinitro-N,N-dipropyl-p-toluidine (trifluralin) + 2,4-D IPE and 2,3,5-trichloro-4-pyridinol (pyrichlor) + (2,4-dichlorophenoxy) acetic acid propylene glucobutyl ether ester (2,4-D PGBEE). The rates of application were 0.8 , 0.75 , $(0.6 + 0.8)$, $(0.2 + 0.5)$ kg per ha, respectively. The performance of these herbicides were compared to that of the control and the granular formulation of amiben applied at 2 kg per ha.

Exp. 8. Mode of action. In this experiment triple carbon-coated rice seeds were treated with herbicides which are commonly used in sorghum, corn, and sugarcane but not rice. The objective was to determine whether activated carbon coating could protect directseeded

rice from any herbicide as long as it was adsorbed by the carbon. The herbicides employed were 2-(2,4-dichlorophenoxy)ethyl sodium sulfate (sesone); N,N-dimethyl-2,2-diphenylacetamide (diphenamid); 2,4-bis (isopropylamino)-6-(methylthio)-s-triazine (prometryne); 3-(hexahydro-4,7-methanoindan-5-yl-)-1,1-dimethylurea (norea); 3-(3,4-dichlorophenyl)-l,l-dimethylurea (diuron); 2-(ethylamino)-4-(isopropylamino) -6-(methylthio)-s-triazine (ametryne) and 2-chloro-4-(ethylamino)-6 isopropylamino)-s-triazine(atrazine). They were applied at the rates of 3.3, 6.7, 2.2, 3.3, 2.2, 3.3 and 3.3 kg/ha, respectively. The performance of triple carbon-coated seed treated with these herbicides was compared to the control and standard amiben treatment.

Exp. 9. Quality of activated carbons. Recent findings of Jordan and Smith (1971) indicated that there were many other activated carbons which proved to be more efficient than Darco G-60 in adsorbing herbicides. These carbons were MCB petroleum base, Norit A Alkaline, Fisher coconut, Witco 249, Mallinckrodt, Norit F. Q. P., Nuchar C-190-N, Nuchar C-1000-N and Norit A neutral. Two of these carbons, Norit A Alkaline (hereinafter is referred to as Norit A) and Witco 249, were obtained and compared to Darco G-60. They were coated on rice seed three times using 50 percent polyvinyl acetate as an adhesive. The coated seeds were sown at the rate of 30 seeds per pot. Uncoated seeds were not sown. Instead, the performance of the carbon-coated seeds was compared to the control. Amiben, CP 53619 and RP 17623 were applied at the rates of 2.24, 3.36 and 3.36 kg/ha, respectively.

Field Experiments

Exp. 1. Seeding rates. A field experiment was carried out in the Paddy-Crop Experiment Station, Kauai, on April 7, 1971 to study the effect of seeding rates on the survival, growth and grain yields of triple carbon-coated rice seed in soil treated with the toxic preemergence herbicides; amiben, CP 53619 and RP 17623. The seeding rates varied from 40 to 200 kg/ha with 40 kg/ha increments. The rates of herbicide application were 2.24, 1.65 and 3.36 kg/ha for amiben, CP 53619 and RP 17623, respectively. The design of the experiment was split plot with herbicides as main plots and seeding rates as subplots. The subplot size was 1.7×2.7 m. The treatments were replicated three times.

Rice seed was coated with activated carbon Darco G-60 in a 5-gallon mixer using 50 percent polyvinyl acetate as an adhesive. About 3 kg of pregerminated rice seed was coated at one time. Each pelleting required approximately ⁴⁵⁰ ^g (about lIb) activated carbon and 150 ml 50% polyvinyl acetate. After the seeds were fully coated, they were spread on paper under shade. Excess carbon was removed by sieving the coated seed through a sieve of size 10. After about an hour, the seeds were coated for the second time to increase the thickness of coating. After another hour or so the pelleting process was repeated for the third time. The resulting coated rice seeds were then ready to be sown in the field. The final weights of carbon coatings ranged from 9 to 14 mg per seed, with an average of about 11 mg per seed (oven dry basis).

The time of sowing was originally planned on April 6 but due to extreme bad weather, sowing was postponed until the next day. The weather at sowing and the next seven days was characterized by light showers and lack of sunshine. The field was flooded 8 days after sowing when the seedlings were at 2 to 3 leaf-stage. The performance of triple carbon coated seeds was compared to control (no herbicide treatment) and to treated uncoated seeds which were sown at the rate of 120 kg/ha, a standard sowing rate practiced in the United States and Australia (Grist, 1962).

Exp. 2. Rates of application. The effect of 2 rates of amiben, CP 53619 and RP 17623 and one rate of sesone on the survival, growth and grain yield of triple carbon-coated rice seed was studied in the field by employing some of the methods established in the greenhouse. The rates of herbicide application were 2.24 and 4.48 kg/ha amiben, 2.24 and 4.48 kg/ha CP 53619, 2.24 and 4.48 kg/ha RP 17623 and 3.36 kg/ha sesone. The design of the experiment was again split plot with herbicides as the main plots and coated and uncoated rice seed as the subplots. Rice seed was coated with activated carbon three times using 50 percent polyvinyl acetate as an adhesive. The seeding rate was fixed at 100 kg/ha. The performance of the coated seeds was compared to both handweeded and unweeded controls.

The herbicides were applied on September 10, 1971. Rice was sown on puddled soil one day after, to allow sufficient time for the herbicides to equilibrate with soil but not too late when the soil was already hardened. The field was flooded 8 days after sowing.

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Exp. 3. Interaction between bird repellent and herbicide treatments. One of the reasons why California rice farmers prefer sowing seed in water to sowing on puddled soil is to avoid bird damage during seedling establishment (De Haven, 1971). In Wailua valley the bird problem was so serious that even at sowing, 95 percent damage could occur with both carbon-coated seed and uncoated seed sown on puddled soil. The Paddy-Crop Experiment Station was heavily infested with wild ducks (Anas platyrhyncos wyviliana), American coot (Fulica americana) and ring-necked pheasants (Phasianus colchicus) which often came to eat rice seed in early morning or late in the afternoon.

Chemical frightening agents have been used intensively in California and Colorado to repel black birds (Agelaius phoeniceus) and pheasants from damaging rice and corn (De Haven, et al., 1972; Woronecki, et al., 1967; De Grazio, et al., 1971; Schafer and Brunton, 1971; West, 1968; West, et al., 1969). Since many birds involved are beneficial and are protected by State and Federal laws, nonlethal frightening agents are obviously more desirable than lethal agents (Woronecki, et al., 1967). Of 724 chemicals screened as repellents for blackbirds, only 6 satisfied the criteria for high repellency and low toxicity (Schafer and Brunton, 1971). Of these, 4-methylthio-3,5-xylyl methylcarbamate (methiocarb, or known by other names such as DRC-736 and mesuro1) was consistently effective against house sparrows (Passer domesticus), grackles (Quiscalus quiscula), pheasants, tricolored blackbirds (Age1aius tricolor), brownheaded cowbirds (Molothrus ater), and Californian quail (Lophortyx californicus). Although methiocarb immobilized most bird species at 10 mg/kg or below and was toxic to them at higher levels, it required about 420 mg/kg to immobilize pheasants and the LD_{50} was about 1000 mg/kg (West, 1968). West, et al. (1969) used up to 3 percent methiocarb in order to obtain complete protection of sprouting corn from pheasants.

Our earlier field experiments with five fungicides and five insecticides, including methiocarb, which were coated on rice seed at the rates of 1 to 3 percent material (i.e. 1 to 3 g powdered material to 100 g rice seed) prior to coating them with activated carbon, showed considerable promise in protecting rice seed from wild ducks, American coot and ring-necked pheasants at seedling establishment. The untreated seed was nearly completely wiped out, while 90 to 100 percent of the treated rice seeds survived. Further studies were needed to determine which of the above repellents was really effective to repel birds.

The present experiment was conducted with the following objectives: (a) to determine the degree of protection afforded by methiocarb (an experimental bird repellent) with and without activated carbon + adhesive on rice seed at seedling establishment and (b) to evaluate the effect of cold temperature on the toxicity of herbicides on uncoated and triple carbon-coated rice seed.

The herbicides used were 2.24 kg/ha amiben, 2.24 kg/ha CP 53619 and 0.90 kg/ha 2,4-D IPE plus weeded and unweeded controls. The seed treatments were pregerminated rice seed dusted with 3% methiocarb, and triple-carbon-coated pregerminated rice seed which was coated with 3% methiocarb prior to coating with activated carbon Darco G-60. Seeding was carried out on February 8, 1972 at the rate of 100 kg per ha. Herbicides were applied on February 7. The plot size was 2.3 x 6.0 m. The design of the experiment was split plot with

herbicides as the main plots and seed treatments as the subplots. Each treatment was replicated three times.

Exp. 4. Granular herbicides. Four granular preemergence herbicides, CP 53619; 2,4-D IPE; EPTC + MCPA; and trifluralin + 2,4-D IPE, were applied before and after sowing triple carbon-coated seed to determine whether prep1anting application of granular herbicides was more effective than early post-emergence application in terms of seeding survival as well as weed control. The rates of application were 3, 1, 1.75 + 0.7 and 0.6 + 0.8 kg per ha for CP 53619; 2,4-D IPE; EPTC + MCPA; and trifluralin + 2,4-D IPE; respectively. In the first treatments, the herbicides were applied on flooded soil 7 days before sowing. At sowing the soil was drained and then ref100ded again 9 days later after the rice seedlings had reached 2-1eaf stage. In the second treatments, the herbicides were applied on flooded soil when both rice and barnyardgrass had reached 2 to 3-1eaf stage. Originally the herbicides were supposed to be applied 7 days after sowing, but due to low temperatures in winter the growth of the seedlings was so slow that the application was delayed by two days.

Both times of application were synchronized so that sowing was done on the same day. Coated and uncoate d seeds were sown on Feburary 9, 1972 at the rate of 100 kg per ha. To avoid herbicide losses through seepage which was encountered in the previous field experiment with several granular herbicides, galvanized metal squares measuring **1.2** x 1.2 m were used to separate one herbicide treatment from another. Factorial combinations of time of application, coating types and herbicides were arranged in a randomized complete block design with four replications (Plate 4).

PIATE 4. GENERAL VIEW OF THE FIELD EXPERIMENT 4 JUST BEFORE THE GRANUIAR HERBICIDES WERE BROADCAST ON FLOODED, PUDDLED SOIL INSIDE THE GALVANIZED METAL SQUARES.

Visual ratings on crop stand, degree of phytotoxicity and weed control were taken 35 days after sowing. Dry matter of rice and weeds was obtained 95 days after sowing using an 80 em by 80 cm quadrat.

RESULTS AND DISCUSSION

Greenhouse Experiment No. 1

Effects of time of flooding on percent seedling survival and dry weight of triple carbon-coated and uncoated rice seed are shown in Figure 8. Flooding the soil 2 days after sowing (DAS) killed both carbon-coated and uncoated rice seed in pots treated with amiben, CP 53619 and RP 17623. In the control pots the percentage survival of seedlings from coated seed under this treatment was only 63%, while that from uncoated seed was 93%. The difference was highly significant. These data suggest that seedlings from carbon-coated seed would suffer more than those from uncoated seed from early flooding because their radicles and coleoptiles were less developed at 2 DAS as a result of coating. According to Palada and Vergara (1972) the death of seedlings as a result of complete submergence was due to a combination of several factors which caused a reduction of carbohydrate content of the plants. These factors were water temperature, water turbidity, low light transmission and possibly also low oxygen content of the water. Carbohydrate content of the plants was correlated to resistance of the plant to submergence.

The death of seedlings from triple carbon-coated seed in herbicidetreated soils as a result of flooding at 2 DAS could be attributed to a combination of these factors: (a) the decreased resistance of rice

FIGURE 8. PERCENT SURVIVAL AND DRY WEIGHT OF SEEDLINGS FROM UNCOATED AND TRIPLE CARBON-COATED RICE SEEDS UNDER DIFFERENT TIMES OF FLOODING AND HERBICIDE TREATMENTS

seedlings to submergence as a result of the reduction of carbohydrate content, (b) increased herbicide phytotoxicity as a result of increased soil water content (Green and Obien, 1969; Stickler, et al., 1969, Jordan, et al., 1968); (c) exposure of both roots and shoots to herbicides present in soil and water. Exposure of both roots and shoots to herbicides inhibited growth more than either shoots or roots alone (Nishimoto, 1970).

These results clearly indicated that early flooding was extremely detrimental to coated seed. Delaying flooding up to 11 days increased both percent seedling survival and seedling dry weights in all three herbicide treatments (Figure 8). But the effect of flooding at 8 DAS on dry weights was not significantly different from that at 11 DAS, suggesting that the soil could be safely flooded as early as 8 days after sowing. Time of flooding, however, was not very critical in soil treated with CP 53619. Under this herbicide treatment the soil could be safely flooded as early as 5 days after sowing, probably because CP 53619 was less toxic than amiben and RP 17623. Apparently the more toxic the herbicide, the more important it was to delay flooding until the seedlings became firmly established in soil. These results also imply that carbon-coated seed cannot be sown in flooded soil or on poorly drained soil in order to obtain high percentage of seedling survival.

Greenhouse Experiment No. 2

The survival of triple carbon-coated rice seeds was not dependent on the rates of application of amiben, CP 53619 and RP 17623 (Figure 9). A significant reduction in the percent survival (27%) was only observed

FIGURE 9. PERCENT SURVIVAL AND DRY WEIGHT OF SEEDLINGS FROM UNCOATED AND TRIPLE CARBON-COATED RICE SEEDS AT DIFFERENT RATES OF AMIBEN, CP 53619 AND RP 17623

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in soil treated with amiben when the rate of application was increased to 4.4 kg/ha. At 1.1 kg/ha both coated and uncoated rice seed survived, because the amounts of amiben and CP 53619 present in soil were not sufficient to kill the uncoated seed. Only 60 to 70 percent of grassy weeds was controlled at this rate. RP 17623 was effective in controlling weeds at 1.1 kg/ha, but quite selective to directseeded rice at this rate as was also reported by Obien, et al. (1971) and Smith and Fox (1971).

The increased phytotoxicity as a result of increased rates of application was, however, shown by the reduction in dry weight of seedlings treated with amiben and RP 17623 (Figure 9 and Plate 5). Both plant height and number of tillers were significantly lower than those seedlings treated with lower rates of application. Coated seed treated with 4.4 kg/ha CP 53619 did not show a significant reduction in dry weight because the seedlings were able to recover quickly from the injury. Thus it can be concluded that the less toxic the herbicide, the less dependent the triple carbon-coated rice seeds were when rates of application up to a certain level were used. As in the previous greenhouse experiments amiben was consistently most toxic, RP 17623 moderately toxic, and CP 53619 least toxic to direct seeded rice.

Greenhouse Experiment No. 3

Percent seedling survival and seedling dry weights of both coated and uncoated seed at different times of application of amiben, CP 53619 and RP 17623 are presented in Figure 10. Herbicide application two days before sowing significantly decreased percent survival of seedlings treated with amiben, but with RP 17623 seedling survival was significantly higher than when the herbicide was applied at sowing. The former was

PIATE 5. THE EXTENT OF GROWTH REDUCTION OF RICE SEEDLINGS FROM TRIPLE CARBON-COATED RICE SEED COMPARED TO THE CONTROL WHEN THE RATE OF AMIBEN APPLICATION WAS INCREASED FROM 1 LB/ACRE (1.12 KG/HA) TO 4 LB/ACRE (4.48 KG/HA). NOTE THAT THE UNCOATED SEED SOWN IN THE BACKGROUND WAS MOSTLY KILLED.

FIGURE 10. PERCENT SURVIVAL AND DRY WEIGHT OF SEEDLINGS FROM UNCOATED AND TRIPLE CARBON-COATED RICE SEEDS AT DIFFERENT TIMES OF APPLICATION OF AMIBEN, CP 53619 AND RP 17623

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probably due to leaching of some amiben, while the latter was probably due to adsorption of some RP 17623 on soil. Amiben is highly soluble in water and highly mobile in soil (Linscott, et al., 1969; Talbert, al., 1970). RP ¹⁷⁶²³ is highly insoluble in water (water solubility 0.7 ppm) and therefore was not expected to be mobile in soil. Herbicide mobility is generally influenced by water solubility, adsorption, flow rate and amount, rates of pesticide application, degradation, and formulation (Helling, 1970).

Percent seedling survival was not significantly affected by preplanting application of CP 53619, probably because the herbicide was not very toxic to triple carbon-coated seed. However, the three herbicides significantly reduced both percent survival and seedling dry weight of coated and uncoated seed when they were applied two days after sowing (Figure 10). The lethal injury can be attributed to the uptake of the herbicides by coleoptiles and/or radicles before they could be adsorbed by carbon coatings. The data suggest that time of herbicide application is not flexible as far as percent survival and dry weight are concerned. In another experiment where sprouted coated seeds (as a result of poor storage) were sown on treated soil, percent survival was also greatly reduced, indicating that it was essential to allow at least ^a ²⁴ hr interval between herbicide application and the emergence of radicles and coleoptiles so that the amount of herbicides around the coated seed could be reduced below the threshold level before they caused permanent injury to the young seedlings.

Greenhouse Experiment No. 4

Herbicide incorporation had no significant effect on percent seedling survival and seedling fresh weights of carbon-coated seed, but significantly increased those of the uncoated seed compared to surface application (Figure 11). The significant increase in seedling survival and fresh weight of uncoated seed was obtained with CP 53619 and RP 17623 but not with amiben. This increase was accompanied by poor weed control with CP 53619, as indicated by the survival of some barnyardgrass seedlings.

Upchurch (1966) reviewed the importance of herbicide placement in soil with a purpose of reducing unfavorable effects of excessive volatility and/or photodecomposition or increasing the contact of herbicide with the zone of entry of germinating weeds. But Hauser (1965) and Ashton (1961) reported that incorporation often resulted in decreased weed control with some herbicides, presumably due to dilution effect. The increased survival of uncoated rice seed and/or the decrease in weed control with CP 53619 and RP 17623 could be attributed to dilution of herbicides when they were incorporated in soil. Weed control effectiveness of RP 17623 was not reduced because it was applied at high rates. If it had been applied at low rates (1.1-2.2 kg/ha) as was CP 53619, its effectiveness probably would have been reduced too.

The survival and growth of seedlings from carbon-coated and uncoated rice seed were surprisingly little affected by soil incorporation of amiben. Incorporation might have diluted amiben concentration in soil as found by Sommerville and Wax (1971),

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FIGURE 11. PERCENT SURVIVAL AND FRESH WEIGHT OF SEEDLINGS FROM UNCOA.TED AND TRIPLE CARBON-COATED RICE SEEDS UNDER TWO METHODS OF APPLICATION OF AMIBEN, CP 53619 AND RP 17623

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but at the same time increased the exposure of rice roots to this herbicide. The total effect was therefore not expected to change amiben toxicity to rice seedlings. The primary site of uptake of amiben is in the root region (Knake and Wax, 1968).

Greenhouse Experiment No. 5

Effect of amiben and CP 53619 on percent seedling height reduction of triple carbon-coated rice seed planted at different spacings is shown in Figure 12. At two weeks after herbicide application there was a dramatic decrease in herbicide toxicity when coated seed was planted at a spacing of 1 x 1 em in both herbicide treatments. Compared to wider spacings seedlings treated with CP 53619 showed no significant difference in height when the seeds were planted at either 1×1 cm or 2×2 cm. In the subsequent weeks there was remarkable recovery of the injured seedlings. The degree of toxicity of herbicides and the seed spacings determined the rate of recovery. The recovery rate was faster in plants planted at close spacings than in wide spacings, and in plants treated with CP 53619 than in plants treated with amiben (Figure 12). All seedlings treated with CP 53619 completely recovered 21 days after sowing, irrespective of spacing, and height differences among the spacings at this stage were not significant.

The toxicity of amiben to coated seed persisted up to 21 days after sowing. Coated seed spaced 1 x 1 and 2 x 2 em completely recovered at 35 days after sowing. Coated seed spaced 3 x 3 and 4 x 4 em showed about 50% height reduction at 7 days after sowing.

FIGURE 12. EFFECT OF AMIBEN AND CP 53619 ON THE HEIGHT OF SEEDLINGS FROM CARBON-COATED SEEDS PIANTED AT DIFFERENT SPACINGS

The height reduction effects disappeared rapidly with time, but at ³⁵ days after sowing the seedlings were still about 20% shorter than the control.

The dry weights of shoots and roots at different spacings are shown in Figure 13. Although the top growth completely recovered, root dry weights still showed significant differences among the various spacing treatments at 35 days after sowing. These results suggest that root and shoot recovery did not occur simultaneously, but rather one followed the other. The root dry weights of seedlings treated with amiben were significantly lower than those seedlings treated with CP 53619. This was in agreement with results obtained earlier in the laboratory.

These results indicated two general trends:

a. Most injured rice seedlings in flooded soil generally recovered with time. The recovery was indicated by an increase in plant height as well as ti1lering of the plants. This trend was observed not only in this experiment but also in other experiments carried out in both greenhouse and the field. The rate of recovery, however, was dependent on the degree of toxicity.

b. The advantage of close spacings in terms of percent seedling survival was not significant. Seedling survival of coated seeds at different spacings ranged from 80 to 97%; these levels were considered satisfactory. In terms of rate of recovery and dry weights of seedlings, only spacings as close as 2×2 cm were significant in reducing herbicide toxicity. Wider spacings showed no clear advantage, especially with amiben. This means that doubling the normal seeding rates (100-120 kg/ha) is not expected to reduce

FIGURE 13. DRY WEIGHTS OF SHOOT AND ROOT OF SEEDLINGS FROM TRIPLE CARBON-COATED RICE SEED UNDER DIFFERENT SPACINGS AND HERBICIDE TREATMENTS

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herbicide toxicity significantly, unless the distribution of the seeds in soil is so uneven as to cause some seeds to cluster closely together. A group of seeds placed near each other would be expected to recover faster from herbicide injury than the same number of seeds spaced wide apart.

Greenhouse Experiment No. 6

Percent seedling survival and seedling dry weights of coated and uncoated seeds in Wai1ua, Wai1ua + Hanalei (1:1), Hanalei and Hanapepe soils are shown in Figure 14. Although there were measurable differences in pH of the four soils in 1 to 1 soil/water ratio, upon flooding the pH of the four soils generally approached 7.0, which was in agreement with published data for other lowland soils (International Rice Research Institute, 1967). Any differences in seedling survival and dry weight in the four soils can be attributed to differences in organic matter content, CEC and clay content only.

Analysis of variance of seedling survival and dry weight indicate that the effects of soils, soils and herbicides interaction, and soils and coatings interaction were not significant.

With a decrease in organic matter content from 12% to 5% there was actually a decrease in percent survival and dry weight of seedlings treated with RP 17623 but the differences were not significant because of relatively large experimental errors. Many workers (Sheets, et al., 1962; Upchurch and Mason, 1962; Harris and Sheets, 1965; Day, et al., 1968) found an inverse correlation between herbicide toxicity and organic matter and/or cation exchange capacity.

FIGURE 14. PERCENT SURVIVAL AND DRY WEIGHT OF SEEDLINGS FROM UNCOATED AND TRIPLE CARBON-COATED RICE SEEDS IN FOUR LOWIAND SOILS AND THREE HERBICIDE TREATMENTS

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Herbicides in Hanalei and Hanapepe soils were probably more available to coated seed because of their low organic matter contents and cation exchange capacity, but seedling establishment in these soils was faster than in Wailua soil due to the absence of minute earthworms which often disturbed the surface layer of Wailua soil. However, the problem of increased herbicide toxicity due to organic matter and/or CEC, if it exists, can be overcome by reducing the rate of herbicide application.

Greenhouse Experiment No. 7

Preplanting application of granular herbicides at 7 days before sowing appeared to be very effective in obtaining both high seedling survival of coated seed and weed control. Figure 15 indicates that granular formulations of $2,4-D$ IPE, EPTC + MCPA, trifluralin + $2,4-D$ and pyrichlor + 2,4-D PGBEE killed about 80 percent of uncoated seed but only 10 to 45 percent of triple carbon-coated seed. These differences were significant. EPTC + MCPA was rather toxic to coated seed, as shown by high mortality of coated seed and high reduction in fresh weight even at 35 DAS.

TCE-styrene was not effective in controlling grassy weeds at 0.75 kg/ha, and uncoated seeds treated with herbicide also survived with no apparent injury. In soil containing 2% organic matter in the Philippines, TCE-styrene applied at 0.75 kg/ha was highly effective in controlling barnyardgrass in transplanted rice (IRRI, 1969). Higher rates than 0.75 kg/ha were probably needed in the high organic matter Hauula paddy soil.

FIGURE 15. PERCENT SURVIVAL AND FRESH WEIGHT OF SEEDLINGS FROM UNCOATED AND TRIPLE CARBON-COATED RICE SEEDS UNDER DIFFERENT GRANUIAR HERBICIDE TRFATMENTS

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Granular formulation of amiben did not perform well under this unique water management system, resulting in poor weed control as well as a high survival of uncoated seed (Figure 15). Part of the explanation can be traced to the loss of much of the applied amiben during the removal of water just before sowing (i.e. 7 days after herbicide application). Amiben, being a highly mobile herbicide (Harris, 1967), was easily removed with the drainage water. This was confirmed in another experiment where several granular herbicides were applied to soils flooded with 2 levels of water: 3 and 7 em. More herbicide losses were observed from soils flooded with 7 em of water than from soils flooded with only 3 em of water, since more water was removed during the drainage in the former treatment than in the latter treatment. Under the same water treatment, losses from herbicides which were less strongly adsorbed on soil would be expected to be greater than those from highly adsorbed herbicides.

Herbicide loss during drainage was one of the disadvantages of the water management used in this study. In the field experiment which will be described later the preplanting application of granular herbicides was compared to early postemergence application in which herbicides losses during drainage were avoided.

Greenhouse Experiment No. 8

Of the seven herbicides tested, only coated seeds treated with sesone survived (Figure 16). Both coated and uncoated seeds treated with diuron, norea, atrazine, ametryne and prometryne survived for the first 10 days after the application; thereafter, the seedlings started to suffer from chlorosis and finally died completely about a

FIGURE 16. THE PERFORMANCE OF UNCOATED AND TRIPLE CARBON-COATED RICE SEEDS IN SOIL TREATED WITH HERBICIDES NOT COMMONLY USED FOR RICE AS MEASURED BY PERCENT SURVIVAL AND DRY WEIGHT OF SEEDLINGS

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week later. Thirty three percent of the coated seeds survived from diphenamid, but the surviving seedlings were severely stunted and showed no sign of recovery. The data suggest that carbon coating could not be expected to protect rice seeds from all herbicides.

Atrazine (Obien, 1970; Jordan and Smith, 1971; McGlamery, 1965), ametryne (Yamane and Green, 1972) and diuron (Jordan and Smith, 1971) have been shown to be highly adsorbed on activated carbon. Atrazine was tightly adsorbed by carbon as evidenced by the small amounts of atrazine desorbed by water (Obien, 1970). Adsorption of norea, diphenamid and prometryne on activated carbon has not been reported, but it can be assumed that these organic compounds would also be as highly adsorbed on carbon as the other triazine or substituted urea compounds. Activated carbon is a non-specific adsorbent for various organic compounds (Hassler, 1963).

The failure of activated carbon coating to protect rice seeds from the above herbicides cannot therefore be attributed to the inability of the carbon to adsorb the compounds, but rather to other factors. Experiments conducted in the Philippines indicated that ametryne and prometryne were highly toxic to transplanted rice even when they were applied at 0.5 kg/ha (International Rice Research Institute, 1965). In a separate experiment where atrazine was applied to different ages of rice seedlings, it was found that rice did not show any tolerance to the herbicide up to 24 days old (Figure 23). Transplanted rice was probably also very susceptible to diuron, diphenamid and norea at the rates used to control weeds, since to date there has been no report regarding the application of these herbicides in transplanted rice. The inability of rice seedlings

to gain "resistance" to the applied herbicides with increasing age was probably the main reason why activated carbon failed to protect rice from the above herbicides. Activated carbon removed herbicide just around the rice seed. The herbicide present away from the seed could enter rice seedlings when the roots started to develop. Also, when the soil was flooded it enabled the herbicide to be distributed all over the soil. The resistance of rice seedlings to the applied herbicide at this stage was indeed crucial in determining the effectiveness of coated seed. This was demonstrated by the ability of seedlings from carbon-coated seed to withstand injury caused by sesone. Thirty-one percent of the coated seeds were killed by sesone, and the remaining survived and showed poor development of roots and shoots. Sesone inhibited roots more than the shoots; this also occurs with other phenoxy compounds, to which sesone belongs. The injured seedlings, however, gradually recovered and at harvest their dry weights were not significantly different from those of amiben-treated seedlings since phenoxy herbicides are selective to transplanted rice (Smith, 1970; De Datta, et al., 1971).

Greenhouse Experiment No. 9

The comparative efficiency of the three types of activated carbons-Darco G-60, Norit A and Witco 249 - in protecting rice seeds from toxic amiben, CP 53619 and RP 17623 is presented in Figure 17. These data indicated that the effectiveness of Norit A as a pelleting material far exceeded that of Darco G-60 and Witco ²⁴⁹ in all the herbicide treatments. The dry weight of either roots or shoots from

FIGURE 17. COMPARISON AMONG THREE TYPES OF ACTIVATED CARBON IN THEIR ABILITY TO PROTECT DIRECTSEEDED RICE FROM AMIBEN, CP 53619 AND RP 17623 AS MEASURED BY DRY WEIGHTS OF SHOOT AND ROOT

seeds coated with Norit A was significantly higher than that from seeds coated with either Darco G-60 and Witco 249, despite the lack of significant differences among the seedling survival of the three carbons. Seedling survivals ranged from 80 to 96 percent. The superiority of Norit A compared to the other two carbons was due to the ability of its seedlings to recover from herbicide injury very quickly, suggesting that Norit A coating was able to adsorb more herbicides than either Darco G-60 or Witco 249. The performance of Darco G-60 was as poor as that of Witco 249.

These results were contrary to what Jordan and Smith (1971) obtained in their adsorption study with these three carbons. They noted that the adsorption of atrazine and diuron on Witco 249 far exceeded Norit A and Darco G-60. Adsorption studies conducted by the author on these carbons confirmed the firidings of Jordan and Smith (Table 39). A close look at coating properties of these three carbons indicated that Witco 249 had relatively poor coating in terms of coating weight and coating quality due to the larger size of its particles (Table 23). Coarse activated carbon such as Witco 249 was not easily coated on rice seed even with large addition of adhesive and/or additional pe11eting. For excellent coatings mesh size should be ideally greater than 200. Rice, in fact, was more easily coated with Norit A than Darco G-60 because Norit A particles were finer. This was second evidence to show that adsorption capacity was not the only criterion for determining the degree of protection afforded by adsorbent coatings. Coating quality and the amount of adsorbent which can be coated on seed were also equally important.

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TABLE 23. PROPERTIES OF ACTIVATED CARBONS DARCO G-60, NORIT A AND WITCO 249 AS COATING MATERIALS FOR RICE SEEDS

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The decrease in herbicide toxicity as a result of the increase in coating weight had been demonstrated by increasing the number of coating layers to three. With very toxic herbicides such as amiben it was also found in ^a separate experiment that complete protection could be achieved when the seed was covered with 200 to 400 mg of activated carbon Darco G-60.

Field Experiment No. 1

The number of seedlings surviving per square meter at different seeding rates and herbicide treatments is shown in Figure 18. Seedling survival of the control was considerably lower than expected, since one of its replication located in the lower end of the experimental field was improperly drained at sowing resulting in the death of many coated seeds. However, with increased seeding rates there was generally an increase in the number of surviving seedlings per square meter. At high seeding rates (160-200 kg/ha) a larger number of coated seeds was killed by amiben and RP 17623 compared to lower rates, but total seedling survival was still comparable to the control. The survival of coated seeds in the three herbicide treatments ranged from as low as 73% with RP 17623 to as high as 127% with CP 53619. The higher number of surviving seedlings in CP 536l9-treated plots than in the control plots was due to low toxicity of CP 53619 coupled with the death of many seeds in one of the replications of the control treatment. In contrast, the survival of uncoated seeds was only 44, 32 and 9 percent in plots treated with CP 53619, Amiben and RP 17623, respectively. The differences between seedling survival of coated and uncoated seeds at the same seeding rate were highly significant.

FIGURE 18. THE SEEDLING SURVIVAL PER SQUARE METER OF UNCOATED SEED SOWN AT 120 KG/HA AND TRIPLE
CARBON-COATED SEED SOWN AT DIFFERENT SEEDING RATES UNDER AMIBEN, CP 53619 AND RP 17623 TREATMENTS

RP 17623 was more toxic than either amiben or CP 53619, as can be seen from large height reduction of seedlings from coated and uncoated seeds treated with these herbicides (Table 24). Amiben was less toxic in this field experiment compared to the previous greenhouse experiments, presumably due to losses of some of this herbicide during the first week after sowing. Frequent rains during this period might have removed some of the amiben since the herbicide was fairly mobile and the levees were not closed to prevent rain water from flooding the field. Early flooding would kill most of the germinating coated seeds (Figure 8).

Toxicity symptoms of the three herbicides in the field were similar to those symptoms observed in the greenhouse.

Significant reduction in plant height among the various seeding rates was only observed at 14 DAS and 40 DAS (Table 24). In plots treated with amiben and RP 17623 coated seeds sown at high seeding rates (120-200 kg/ha) were about 8 to 17 percent taller than the same seeds sown at lower seeding rates. There was apparently a considerable reduction in herbicide toxicity with an increase in seeding rates up to 200 kg/ha, although in the greenhouse such a response would not be expected. The discrepancy can be explained in terms of uneven distribution of coated seeds in soil in the field. Some seeds tended to stay close to each other when they were broadcast on soil. Seeds spaced 2 em or less had a better chance of overcoming herbicide toxicity (Figure 12). Furthermore, total carbon applied in soil was increased from 13.3 to 66.7 kg/ha when seeding rates were increased from 40 to 200 kg/ha (Table 25). With an increase in carbon/herbicide ratio, total herbicide available to each seed/seedling would be

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TABLE 24. DEGREE OF TOXICITY AND WEED CONTROL OF AMIBEN, CP 53619 AND RP 17623 AT DIFFERENT SEEDING RATES OF TRIPLE CARBON-COATED RICE SEED

*Assuming 100 seeds weight 3 gm

**Assuming weight of carbon per seed is 10 mg

***Assuming uniform distribution of both herbicide and the seeds, and no degradation and soil adsorption taking place

expected to decrease due to large adsorption of the herbicide on carbon (Jordan and Smith, 1971).

The three herbicides controlled most of the annual weeds effectively (Table 24). The most common weeds in flooded soil in Wailua were Echinochloa crusgalli, Jussiaca suffruticosa and Cyperus difformis, representing grasses, broadleafs and sedges, respectively. Weed control was rated 30 days after sowing just before the control plots were handweeded. Plots treated with CP 53619 were not completely free from weeds. Few grassy and broad1eaf weeds still survived. Persistence of amiben in soil apparently only lasted for about 8 weeks, for at the end of 8 weeks the treated soil which was left bare due to death of coated or uncoated seeds, was heavily infested with Cyperus difformis. Plots treated with RP 17623 remained clean until harvest time, indicating the long persistence of this herbicide in soil. The half-life of RP 17623 varies from 4 to 6 months (Anon., 1972).

Although most of injured seedlings completely recovered at 70 DAS, the flowering of these seedlings was delayed by about 2 to 7 days depending on the degree of toxicity. The differences in flowering time necessitated the delay in harvesting the rice up to 35 days after flowering. Nangju and De Datta (1970) reported that optimum time of harvest of rice in the dry season in the Philippines was about 30 days after flowering. Early harvest was recommended when the plants lodged, as in this experiment. When total number of tillers per square meter exceeded 500 (Figure 19), the rice plants invariably

FIGURE 19. THE NUMBER OF TILLERS PER SQUARE METER OF UNCOATEI SEED SOWN AT 120 *KG/HA.* AND TRIPLE CARBON-COATED SEED SOWN AT DIFFERENT SEEDING RATES UNDER AMIBEN, CP 53619 AND RP 17623 TREATMENTS

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lodged a few days after flowering due to intense interspecific and intraspecific competition and especially at high nitrogen levels (Tanaka, et al., 1964). All the coated seeds sown at 160 \lg/ha or higher and the uncoated seeds of the control plot lodged heavily, resulting in reduction in grain yields (Figure 20). IR8 is a high tillering variety, and therefore produced a lot of tillers when given large amount of fertilizers and/or larger spacing. Lodging could be avoided by reducing the rate of nitrogen fertilizers (De Datta, Tauro and Balaoing, 1968).

On the basis of grain yield, optimum seeding rate of coated seeds for the control, amiben and RP 17623 was 120 kg/ha, except for CP 53619 which was 40 kg/ha (Figure 20). Lower seeding rates than 120 kg/ha for the control, amiben and RP 17623 could be used since grain yield differences between seeding rates of 80 and 120 were not significant. The optimum seeding rate of CP 53619 appeared to be equivalent to that of transplanted rice made in a dapog seedbed (R. I. C. E., 1967). The low seeding rate was made possible by the high total seedling emergence coupled with minimal herbicide injury.

Field Experiment No. 2

Percent mortality and height reduction of coated and uncoated rice seed in soil treated with two rates of amiben, CP 53619 and RP 17623 and one rate of sesone are presented in Table 26. In all cases, many of the coated and uncoated rice seeds were either killed or severely injured by the herbicides, although the percent mortality and/or the degree of toxicity were proportionately higher with uncoated seeds than coated seeds. The relatively high percent mortality of

FIGURE 20. GRAIN YIELDS OF UNCOATED SEED SOWN AT 120 KG/HA AND TRIPLE CARBON-COATED RICE SEED SOWN AT DIFFERENT SEEDING RATES UNDER AMIBEN, CP 53619 AND RP 17623 TREATMENTS

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TABLE 26. THE NUMBER OF SURVIVAL AND PERCENT HEIGHT REDUCTION OF PIANTS FROM TRIPLE CARBON-COATED AND UNCOATED SEEDS AT DIFFERENT GROWTH STAGES IN SOIL TREATED WITH AMIBEN, CP 53619, RP 17623 AND SESONE

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a) $U =$ Uncoated rice seed

 $b)$ _C = Triple carbon-coated rice seed
coated rice seed in this experiment was attributed to several factors: (a) poor drainage, (b) horizontal or downward growth of co1eopti1es instead of upward growth away from soil surface, (c) uneven coating thickness of seeds made in a 5-gal1on mixer. The most important factor was probably poor drainage, since a 1 to 2 em layer of water present around the pregerminating coated seeds was fatal to them. In a farmer's field a drainage problem would be much more serious, since the land preparation is generally seldom as good as that in a small field experiment.

As before, CP 53619 was the least toxic among the four herbicides even when the rate of application was increased to 4.48 kg/ha. Mortality was lower and rate of recovery was generally faster with seeds treated with CP 53619 than the other herbicides (Table 26). Amiben and RP 17623 were very toxic to both coated and uncoated rice seeds. At 4.48 kg/ha only about 10% of uncoated seeds and 50% of coated seeds survived from these two herbicides, and the injury was still observed up to ⁷⁰ DAS, while other seedlings had generally recovered completely. Sesone killed nearly all of the uncoated seeds (except a few outside the sampling areas) and 43% of the coated seeds. Rice seeds are extremely sensitive to all phenoxy compounds including sesone and 2,4-D IPE, especially at the germination stage. Seed exposure caused more injury than either root or shoot exposure at a given rate of herbicide (Gray and Weierich, 1969). However, sesone did not control grassy weeds effectively presumably due to the absence of flooding shortly after the application. Sesone did not persist in soil very long either, since after about 5 weeks the treated bare soil was infested with weeds. Seedling stands of rice

treated with 4.48 kg/ha amiben and 3.36 kg/ha sesone are shown in Plates 6 and 7, respectively.

The yield components and grain yields of both coated and uncoated rice seeds are shown in Table 27 and Figure 21, respectively. The weeded control produced 4.2 to 4.7 metric tons/ha which was almost twice that of the unweeded control. The large reduction of grain yield of the unweeded control was due to the large number of barnyardgrass seeds sown at sowing to increase the uniformity of weed infestation. The grain yield of the weeded control, however, was far lower than the maximum grain yields obtained in the previous field experiment. The reduction can be attributed to differences in solar radiation received by the two crops during the last 45 days before harvest (Moomaw, Baldazo and Lucas, 1967). The first crop was harvested in August 1971 and the second crop in January 1972. Solar radiation in January was about one-half of that recorded in August (Figure 3).

The grain yields of coated seeds in all the herbicide treatments ranged from 4.0 to 5.0 ton/ha which were not significantly different from the control (Figure 21). The grain yields of uncoated seeds treated with both rates of CP 53619 and low rates of amiben and RP 17623 were comparable to the weeded control because the high mortality of the seeds was compensated for by larger tiller production per hill (Table 27). Only uncoated seeds treated with 4.48 kg/ha amiben, 4~48 kg/ha RP 17623 and 3.36 kg/ha sesone produced significantly lower grain yields than the weeded control. Their flowering was also delayed by 5 to 8 days. The reduction in grain yields of these treatments was due to extremely high mortality of the uncoated seeds

PIATE 6. POOR STAND OF SEEDLINGS FROM UNCOATED RICE SEED IN THE FOREGROUND IN CONTRAST TO EXCELLENT STAND OF SEEDLINGS FROM CARBON-COATED SEED IN THE BACKGROUND AT 70 DAS WHEN BOTH SEEDS WERE TREATED WITH 4.48 KG/HA AMIBEN.

PIATE 7. EXCELLENT STAND OF SEEDLINGS FROM TRIPLE CARBON-COATED SEED IN THE BACKGROUND, WITH COMPLETE KILL OF UNCOATED SEED IN THE FOREGROUND WHEN BOTH SEEDS WERE TREATED WITH 3.36 KG/HA. SESONE.

TABLE 27. EFFECT OF THO RATES OF AMIBEN, CP 53619 AND RP 17623, AND ONE RATE OF SESONE ON SOME OF THE YIELD COMPONENTS OF PLANTS FROM TRIPLE CARBON-COATED AND UNCOATED RICE SEEDS

a) $U =$ Uncoated rice seed

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 (b) _C = Triple carbon-coated rice seed

FIGURE 21. GRAIN YIELDS OF UNCOATED AND TRIPLE CARBON-COATED RICE SEEDS IN SOIL TREATED WITH TWO RATES OF AMIBEN, CP 53619 AND RP 17623 AND ONE RATE OF **SESONE**

 $\mathcal{L}^{\text{max}}_{\text{max}}$

 $\sim 10^6$

 $\sim 10^{-11}$

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which could not be adequately compensated with large production of either tillers or panicles.

Field Experiment No. 3

The mortality of uncoated and coated seeds due to birds and herbicides was differentiated by counting the number of seeds at sowing and a week after sowing at a predetermined sampling area, and by counting the number of seedlings surviving in the control plots and treated plots two weeks after sowing. The results are presented in Table 28. One of the drawbacks of determining bird damage using this procedure was the difficulty in accounting for all the seeds sown on puddled soil since some of them were undistinguishable from the dark colored mud, and hence were not counted. Percent mortality of seeds coated only with methiocarb was generally 4 to 6 percent higher than seeds coated with both methiocarb and activated carbon Darco G-60 using 50% PVA as an adhesive. The differences, however, were not significant. Without an adhesive the insecticide could probably have dispersed in water, thus reducing its effectiveness as ^a bird repellent. Methiocarb was also found to be rather toxic to rice when it was dusted without activated carbon. Although seed mortality due to birds ranged from 5 to 15%, the actual bird damage might have been lower since not all the remaining seeds could be accounted for. Considering this factor, it could be safely concluded that methiocarb was extremely effective in repelling birds at seedling establishment. These results confirm the findings of West, et al. (1969). With the use of this bird repellent, it is now possible to conduct experiments on directseeded flooded rice without installing

TABLE 28. PERCENT MORTALITY OF COATED AND UNCOATED RICE SEED DUE TO BIRDS AND HERBICIDES IN RICE PELLETED WITH ACTIVATED CARBON AND/OR METHIOCARB

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bird-proof net before sowing. This net, however, is still required from flowering up to harvesting stage, since no effective method has been developed for repelling hundreds of rice birds during this period. De Haven, et al. (1972) claimed that methiocarb reduced blackbird damage to ripening rice in California by about 60 percent when 3.4 to 11.2 kg/ha methiocarb was applied just before ripening of rice grains. The same chemical used here on sorghum and rice and applied at 1.12 to 2.24 kg/ha just after flowering was totally ineffective against rice bird damage (unpublished data of Dimyati Nangju and Rodolfo Escalada). Rice birds, in contrast to blackbirds, normally eat cereal grains when they are still soft, and thus control has to be carried out soon after the crop has flowered. Higher rates of methiocarb were not used because the chemical was insoluble in water.

Seeds coated with both methiocarb and activated carbon were also protected from the preemergence herbicides; amiben, CP 53619 and 2,4-D IPE, although the number of seedling surviving per square meter with the three herbicides was considerably lower than in the previous experiments. Mortality of coated seeds was 32, 59 and 74 percent for CP 53619, amiben and 2,4-D IPE, respectively (Table 28). More than 90 percent of uncoated seeds sown on the same plot was killed.

The high mortality of coated seeds sown in February 1972 can be partly explained by the slow growth of the seedlings as a result of low temperatures during the first two weeks after sowing. In Table 29 growth rate and percent survival of seedlings from coated seeds treated with amiben and CP 53619 and sown at different time of the year are compared. Although in experiment one CP 53619 was applied

 $\sim 10^{11}$ km s $^{-1}$

at 1.65 kg/ha, slightly lower than the rate applied in the other two experiments, survival can be correlated to growth rate of rice seedlings. The growth rate of rice sown on February 8 was 2 to 3 times slower than that of rice sown either in April 6 and September 11, due primarily to low temperatures during growth. Solar radiation, although very low in winter, had no significant effect on growth rate (Table 16). Slow growth rate prolonged the contact of rice seedlings with toxic herbicides which might have caused high mortality of coated seeds observed in this experiment. Penner (1971) and Hammerton (1966), however, reported that herbicide toxicity was generally lower at low temperatures than at high temperatures due to slow rate of herbicide absorption as a result of low metabolic rates. The effectiveness of carbon coating might also be reduced in winter because herbicide adsorption on carbon was generally greater at high temperatures than low temperatures (Weber, 1965).

The high toxicity of amiben, CP 53619 and 2,4-D IPE to coated and uncoated seeds can be used to serve as a model to demonstrate some of the trends observed earlier. Firstly, injured seedlings generally recovered with time. In Figure 22 the heights of treated plants are compared to that of the weeded control. It is significant to note from this figure that rate of recovery was not only dependent on herbicide toxicity and carbon coating but also on the persistence of the herbicide in soil. In term of I_{50} , 2,4-D IPE is more toxic than amiben, but the 2,4-D IPE treated plants were able to overtake the height of amiben-treated plants about 6 weeks after sowing since the persistence of 2,4-D IPE in soil only lasted for about 4 weeks while

FIGURE 22. HEIGHT OF PIANTS FROM UNCOATED AND TRIPLE CARBON-COATED RICE SEEDS AT VARIOUS GROWTH STAGES IN SOIL TREATED WITH AmBEN, CP 53619 AND 2,4-D IPE

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that of amiben lasted for about 8 weeks. Most of the plants, however, recovered from injury at about 10 to 12 weeks after sowing for the coated seeds and about 12 to 15 weeks after sowing for uncoated seeds. This was the period in which growth rate of the control started to slow down, enabling the injured seedlings to approach the height of the control. The data suggest that the response of rice plants to herbicide application should be evaluated at different growth stages. If the evaluation has to be made only once, it probably should be done no later than one month after the application.

In Table ³⁰ the number of tillers, dry matter of rice and weed weight for each coating and herbicide treatments are presented. The unweeded plot was extremely weedy, and its dry matter production was only 30 to 40% of the weeded control. The dry matter production of coated seeds treated with CP 53619 was comparable to that of the weeded control while that of coated seeds treated with amiben and 2,4-D IPE was 30 to 40% lower than the weeded control, but significantly higher than the unweeded control. The stands of rice plants at 95 DAS under amiben and CP 53619 treatments are shown in Plate 8.

Although less than 10 percent of uncoated seeds survived in plots treated with CP 53619 and amiben, dry matter production was only about 50% less than that of coated seeds treated with the same herbicides. This was due to larger production of tillers per hill with uncoated seeds compared to coated seeds (Table 30). The tillering of IR8 appeared to be mainly determined by availability of space, and secondarily by toxicity of herbicides. In 2,4-D IPE-treated plots the uncoated seeds could not tiller as well as the others because

a) $U =$ Uncoated seed + methiocarb

b) $c =$ Uncoated seed + methiocarb + activated carbon

*Harvested at flowering stage of rice (105 DAS)

PIATE 8. IN SPITE OF HIGH MORTALITY OF TRIPLE CARBON-COATED RICE SEEDS SOWN IN WINTER AS RESULT OF AMIBEN (LEFT) AND CP 53619 (RIGHT) TREATMENTS, THE STANDS FROM THESE SEEDS APPEARED EXCELLENT AT 90 DAS DUE TO HIGH TILLERING OF IR8. NOTE THE SPARSE POPUlATION OF SEEDLINGS FROM UNCOATED SEEDS WHICH WERE MUCH MORE SEVERELY INJURED BY THE HERBICIDES COMPARED TO CARBON-COATED SEEDS.

the available space was quickly taken over by weeds which emerged as soon as 2,4-D IPE lost its persistence. Like sesone, 2,4-D IPE was not effective under the water management which favored the survival of coated seeds. Flooding the soil as soon as 2,4-D IPE was applied generally controlled most of the annual weeds (De Datta, Lacsina and Seaman, 1971) but delayed flooding appeared to reduce its effectiveness.

Field Experiment No. 4

Field experiments with granular herbicides were not easily accomplished in the Paddy Crop Experiment Station since proper water management was often disrupted by heavy rains and/or flooding of the whole valley. But field experimentation is the only way to assess the effectiveness of herbicides in controlling weeds growing in their natural habitat. The results presented in Table 31 have to be accepted with some reservations since five days after the first application of the granular herbicides (prep1anting application) the valley was flooded with 0.5 m of water, and three days after the second application (postplanting application) the valley was again flooded with rain water for the second time. That was one of the wettest months recorded for the last three years. Some herbicide losses might have occurred during these two f1oodings.

Despite all this, two general trends can be observed from the data (Table 31). Firstly, prep1anting applications of 2,4-D IPE, CP 53619, EPTC + MCPA and trifluralin $+ 2,4$ -D IPE were generally much more effective in controlling weeds than post emergence applications of the herbicides at the same rates. Granular herbicides

TABLE 31. COMPARISON BETWEEN PREPLANTING AND POSTEMERGENCE APPLICATION OF SOME GRANUIAR HERBICIDES AS MEASURED BY DEGREE TOXICITY TO SEEDLINGS FROM COATED AND UNCOATED RICE SEEDS, AND TOTAL WEIGHT OF WEEDS

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TABLE 31. (CONTINUED) COMPARISON BETWEEN PREPIANTING AND POSTEMERGENCE APPLICATION OF SOME GRANUlAR HERBICIDES AS MEASURED BY DEGREE TOXICITY TO SEEDLINGS FROM COATED AND UNCOATED RICE SEEDS, AND TOTAL WEIGHT OF WEEDS

*Eva1uated at 35 DAS **Harvested at 95 DAS $a)$ U = Uncoated seed $b)$ C = Triple carbon coated rice seed $c)$ DBS = Days before sowing $d)$ DAS = Days after sowing

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controlled weeds more effectively before or just after weeds emerge than when they were already growing (Ahrens, 1972). CP 53619 was the only herbicide showing excellent early postemergence activity. About 90 percent of the barnyardgrass and other weeds were killed about 8 days after the application. Trifluralin $+ 2,4$ -D IPE controlled 30 to 40 percent of the weeds, while 2,4-D IPE and EPTC + MCPA were totally ineffective. De Datta and Bernasor (1970), however, obtained excellent weed control when granular formulations of CP 53619 and 2,4-D IPE were broadcast at 2 to 3 leaf-stage of barnyard grass.

Secondly, coated seeds showed better stands and growth than uncoated seeds when both seeds were treated with the four granular herbicides 7 days before sowing. The superiority of coated seeds over uncoated seeds could still be observed at ⁹⁵ DAS, as shown by significantly greater dry matter yields of coated seeds. The dry matter production of uncoated seeds treated with 2,4-D IPE was the lowest (5.3 ton/ha) since weeds took over the bare soil as soon as the herbicide lost its persistence in soil. The dry matter yields of coated seeds were similar or slightly higher than that of the weeded control.

However, seedlings from both coated and uncoated seeds were equally injured when the four herbicides were applied on flooded soil 9 days after sowing, except in plots treated with CP 53619. With the herbicides present in both water and soil, the coated seeds were not expected to be able to overcome the herbicide toxicity. The dry matter yields of both coated and uncoated seeds under these treatments, except CP 53619, were much lower than that of the weeded control, due to poor weed control.

SUMMARY AND CONCLUSIONS

Nine pot experiments and four field experiments were conducted at the Hawaii Agriculture Experiment Station on Kauai to study factors which affected the performance of triple carbon-coated rice seed in flooded soil. The results obtained from these experiments shed some light as to factors which could improve its performance or limit its effectiveness in protecting rice seed from toxic preemergence herbicides.

The factors which could improve effectiveness of triple carboncoating of rice seeds were as follows:

a. Delaying the time of flooding at least 8 days after sowing increased seedling survival. Early flooding was not critical with a mildly toxic herbicide such as CP 53619, but late flooding was beneficial to highly toxic herbicides such as amiben and RP 17623.

b. Application of herbicides two days before sowing improved the protection by coated seeds from herbicides which were highly adsorbed on soil but not from herbicides which were mobile in soil. Such a preplanting application, however, had to be considered judiciously in the field, since too much delay in sowing would bring about a germination problem due to drying of the soil surface.

c. Herbicide toxicity to coated seed was dependent on rate of application. Greater success in seed pelleting would be obtained if the lowest possible rate was used without sacrificing weed control activity. For amiben and CP 53619 these rates were 2.24 and 1.65 kg/ha, respectively.

d. The benefits of increasing seeding rate of coated seed were to obtain excellent stand, even if many seeds were killed, and to speed up the rate of recovery. In the greenhouse large number of seeds were

needed to overcome amiben toxicity. In the field high seeding rates resulted in intense intraspecific and interspecific competition among the surviving seedlings. Thus, optimum seeding rates had to be determined on the basis of these considerations. Generally, a seeding rate of 100 to 120 kgjha was adequate. At higher seeding rates the rate of nitrogen fertilizer should be reduced to avoid lodging.

e. The performance of coated seeds was vastly improved by the high adsorbent capacity of activated carbon and the weight and quality of coating made from this carbon; the latter was more important than the former. Coating made from activated carbon Norit A was more effective than either Darco G-60 or Witco 249. Witco 249, though an excellent adsorbent, performed very poorly due to poor coating quality. For excellent coating quality the mesh size of carbon should be at least 200, preferably 300 to 400.

Factors which are known to reduce the effectiveness of carboncoated seeds were as follows:

a. Coated seeds broadcast on poorly drained soil - either due to early flooding or poor land preparation - would be instantly killed by toxic herbicides. In the greenhouse flooding 2 days after sowing killed the coated seeds.

b. Herbicides applied just after the coated seeds germinated either killed or severely injured these seeds. Similarly, sprouted coated seeds - either due to poor storage or improper coating - would be killed if they were sown in soil treated with toxic herbicides, due to a lack of time interval between herbicide adsorption by carbon coating and emergence of coleopti1e and radic1es.

c. Carbon coating could not protect rice seeds from preemergence herbicides which proved to be lethal to transplanted rice. This was shown by complete kill of coated seeds by atrazine, ametryne, diuron, prometryne and norea.

d. Among the climatic factors, temperature was most important in affecting the survival of coated seeds. In winter where the low temperature was 63 F (17.2 C) and the high temperature was 76 F (29.4 C), percent survival of coated seed treated with CP 53619, amiben and 2,4-D IPE was reduced by at least 30 to 50 percent compared to spring or summer sowing. The cause of this reduction was not very clear. Slow growth which prolonged the contact between seedlings from coated seed and herbicide, and reduced herbicide adsorption on carbon at low temperatures might be responsible for this high mortality.

Herbicide incorporation and formulation and soil types did not show any effect on the performance of carbon-coated seed. Herbicide incorporation had an undesirable effect with amiben and CP 53619 since weed control activity was reduced due to dilution. Granular formulations of preemergence herbicides caused no problem if they were applied on flooded soil at least a week before sowing. This system worked well with CP 53619, 2,4-D IPE, EPTC + MCPA, trifluralin + 2,4-D IPE and pyrichlor + 2,4-D PGBEE, but not with highly mobile herbicides such as amiben due to herbicide losses during drainage of water. In the field, preplanting applications of granular herbicides were generally more effective than post-planting application because post emergence application did not control the growing weeds. CP 53619, however, showed excellent early postemergence activity when applied at 3.36 kg/ha.

In both greenhouse and the field triple carbon-coated rice seed performed better than ordinary uncoated rice seed in soils treated with amiben, CP 53619, RP 17623, 2,4-D IPE and sesone, at least in terms of the number of seedling surviving per unit area. In terms of grain yield or dry matter yields at harvest, the difference between the performance of coated and uncoated seed was difficult to prove, since (a) IR8, being ^a high ti11ering variety, would tiller readily if more space was given to it, and (b) no matter how severe the injury, if the seedling survived, the chance was it would recover ⁷⁰ to ⁹⁰ days after sowing. The rate of recovery, however, was dependent on availability of the herbicide to the seed/seedling, sensitivity of rice to the herbicide, and the persistence of the herbicide in soil. RP 17623 was the most persistent herbicide in soil, followed by CP 53619, amiben and 2,4-D IPE.

CHAPTER VIII. THE PERFORMANCE OF COATED AND UNCOATED RICE SEED IN UPLAND (NONFLOODED) SOIL

Weed control in upland rice poses a challenge to weed scientists due to heavy infestations of both annual and perennial weeds. Most of the upland rice is grown in developing countries, and weed control is normally done by hand and/or primitive tools. Although chemicals are still new and expensive in these countries, ^a single application of ^a preemergence herbicide will do a much better job than traditional handweeding. Upland rice yielded as much as transplanted rice in a habitat free from weed competition (IRRI, 1968). Many of the excellent preemergence herbicides, however, are toxic to directseeded rice. The objective of this study was to evaluate several methods which might be economically used to overcome herbicide toxicity in upland rice. These methods were:

a. Pelleting rice seed with activated carbon three times,

b. Band application of activated carbon slurry,

c. Placement of activated carbon and vermiculite mixture over the rice seeds, and

d. Placement of rice seeds in soil at different depths.

MATERIALS AND METHODS

Pot Experiment No. 1

Pregerminated rice seeds were planted at a depth of 2.5 em in pots having inside dimensions of 33 em and 50 em and 10 cm deep, with 10 seeds per row. Each pot could accommodate 4 rows. Activated carbon Darco G-60 was applied to each row in 3 ways:

a. by coating rice seeds three times with 50% PVA as an adhesive just before sowing,

b. by suspending activated carbon in water and then applying the suspension in bands of 2.5 cm over the seed at the rate of 90 kg/ha, and

c. by mixing activated carbon and vermiculite in a 1:1 ratio before placing them over the seed in a band 2.5 em wide and 2.5 em deep. The fourth row was planted with ordinary uncoated seed.

Four herbicides representing a wide spectrum of phytotoxicity to directseeded rice were applied one day after sowing. The herbicides were amiben, CP 53619, atrazine and diphenamid. The rate of application was 3.36 kg/ha, except for diphenamid which was 6.72 kg/ha. The design of the experiment was split plot with herbicides as main plots and method of application of activated carbon as subplots. The treatments were replicated three times, and all the plant foliage was harvested 35 days after sowing.

Pot Experiment No. 2

Amiben, CP 53619 and RP 17623 were applied on drill seeded upland rice at the rate of 3.36 kg/ha. Pregerminated rice seeds were planted at four depths: 1.5, 3.0, 4.5 and 6.0 em, to determine whether the phytotoxicity of these herbicides could be reduced simply by increasing depth of sowing. The seeding rate was 10 seeds per one gallon pot. The pots were arranged in a completely randomized design. Dry weights of rice plants were obtained after growing them for 4 weeks.

Field Experiment

Encouraged by the results obtained in pot experiment No.2, a field experiment was conducted at the Paddy-Crop Experiment Station to study the effect of different rates of amiben, CP 53619, RP 17623 and 2,4-D IPE on weed control and phytotoxicity to upland rice.

Pregerminated rice seeds were planted on November 11, 1971 in rows 30 cm apart at the rate of 80 kg/ha. The depth of seeding was fixed at 3 cm. Three rates of amiben $(2, 24, 3.36$ and 4.48 kg/ha), CP 53619 (1.65, 3.36 and 4.94 kg/ha) and RP 17623 (2.24, 3.36 and 4.48 kg/ha), and two rates of $2,4-D$ IPE $(0.90$ and 1.32 kg/ha) were applied two days after sowing. Each treatment was replicated 4 times and the design of the experiment was completely randomized block. The plot size was 2.1 by 2.7 em.

RESULTS AND DISCUSSION

Pot Experiment No. 1

The comparison among methods of activated carbons application under amiben, CP 53619, atrazine and diphenamid treatments is shown in Table 32. The best method of carbon application in terms of percent seedling survival and dry weight appeared to be the placement of 2.5 cm layer of carbon + vermiculite mixture $(1:1)$ over the rice seeds. This technique was very effective even with highly toxic atrazine. This was understandable since nearly 4500 kg of activated carbon and 4500 kg of vermiculite were applied per ha. This amount was more than adequate to intercept all the applied herbicides. Kratky and Warren (197l) also obtained excellent results when a

TABLE 32. COMPARISON AMONG METHODS OF APPLICATION OF ACTIVATED CARBON IN PROTECTING DRILLSEEDED UPLAND RICE FROM AMIBEN, CP 53619, ATRAZINE AND DIPHENAMID

 \mathcal{L}_{max} and \mathcal{L}_{max}

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SEEDLING SURVIVAL (% CONTROL)

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carbon and vermiculite mixture was placed in a hole over cucumber (Cucumis sativus L.) and tomato (Lycopersicum esculentum Mill.) seeds which were treated with simazine. This method, however, was uneconomical for crops like rice. Furthermore, the mixture was easily blown away by wind when it was dry.

Band application of activated carbon and seed pelleting performed as poorly as seeds which were not protected by activated carbon. Apparently some of the herbicides were not adsorbed and still caused severe toxicity through shoot or root adsorption. The failure of activated carbon coating was to be expected since there was no intimate contact between herbicides on soil surface and seeds planted 2.5 em below the surface.

Band application of activated carbon slurry surprisingly did not offer any protection to upland rice, even from amiben. Linscott and Hagin (1966) and Burr, et al. (1972) had applied this method to other upland crops (alfalfa and Italian ryegrass) and found that it was rather effective. Burr, et al. (1972) used 0.5% polyethelene glycol dedecyl ether surfactant (surfactant WK) to suspend activated carbon Aqua Nuchar in water. No surfactant was used at all in this study, and therefore the application might not be uniform.

CP ⁵³⁶¹⁹ was not toxic to uncoated seed when it was not directly exposed to the herbicide as in puddled soil. In upland soil much of the herbicide was probably adsorbed on soil surface and little of it reached the seed. This result was in agreement with IRRI (1969, 1971).

Pot Experiment No. 2

Seeding depth played significant roles in obtaining high survival as well as high dry weight of upland rice as shown in Table 33. Seeds planted at 1.5 cm were not easily killed by amiben, CP 53619 and RP 17623, but their dry weights were significantly lower than the control because their growth was severely inhibited by the herbicides. Sowing the seeds at a greater depth (3.0 to 4.5 em) improved the stand as well as the growth of upland rice even in pots treated with highly toxic amiben. Deeper seeding, however, was undesirable since the percentage of emergence was greatly reduced, as shown by the low percent seedling survival of the control (only 23 percent).

The reduction of herbicide toxicity with depth of sowing can be explained in terms of proximity of herbicide to rice seeds. Amiben, CP 53619 and RP 17623 were leached down to the subsurface soil when the pots were watered every day, and they would be absorbed by either rice shoots or roots depending on the degree of leaching. However, recent study conducted by Nishimoto, et al. (1969) indicated that proximity of atrazine, EPTC and diuron to oats (Avena sativa L.) and green foxtail (Setaria viridis (L .) Beauv) seeds increased the effectiveness of these herbicides. They also found that a narrow concentrated layer of these herbicides adjacent to seed was more effective than a wider dilute layer above or below the seed. From these findings it can be deduced that the reasons why amiben, CP ⁵³⁶¹⁹ and RP ¹⁷⁶²³ were less toxic to seeds planted at 3.0 and 4.5 than at 1.5 em were greater dilution of these herbicides and larger distance between the rice seeds and the placement of the herbicides.

TABLE 33. PERCENT SEEDLING SURVIVAL AND DRY WEIGHT OF RICE SEEDED AT DIFFERENT DEPTHS AND TREATED WITH AMIBEN, CP 53619 AND RP 17623

| Herbicide | Rate | Depth of Seeding (cm) | | | | |
|-----------|---------|--------------------------|-----|-----|-----|------|
| | (kg/ha) | 1.5 | 3.0 | 4.5 | 6.0 | Mean |
| Control | 0 | 97 | 93 | 90 | 23 | 76 |
| Amiben | 3.36 | 50 | 80 | 83 | 3 | 54 |
| CP 53619 | 3.36 | 83 | 97 | 83 | 7 | 68 |
| RP 17623 | 3.36 | 80 | 97 | 83 | 13 | 68 |
| | Mean | 78 | 92 | 85 | 11 | -- |

SEEDLING SURVIVAL (% POSSIBLE)

LSD (0.05)

Field Experiment

Even though no weed seeds were broadcast at sowing the weed population in the control plots were extremely high. Amiben, CP 53619 and RP 17623 treatments resulted in better weed control with increasing rates. At lower rates (1.65 - 2.24 kg/ha) the three herbicides were not very effective in controlling both grasses and other weeds (Table 34). At higher rates weed control by the three herbicides was significantly improved. 2,4-D IPE, as expected, was not very effective in controlling grassy weeds at the rates it was applied.

The toxicity of the four herbicides to upland rice appeared to be determined by the rates of application as well as the degree of leaching. In general, stand and growth rate were decreased by increasing rates of application, but the increase in toxicity was more pronounced with amiben and 2,4-D IPE than with CP 53619 and RP 17623 (Table 34). The high toxicity of amiben and 2,4-D IPE can be attributed to the high mobility of these two herbicides (Figure 25), and the high sensitivity of rice seedlings to these herbicides (Figure 5). The toxicity of these two herbicides was intensified by heavy rains occurring two days after application.

The weed population in each treatment was rated at 50 DAS and the results are presented in Table 35. Completely different species infested upland rice compared to lowland rice, and the number of species was also greater in upland soil than in lowland soil. Of the species listed in Table 35, only Eleusine indica, Echinochloa colonum, Amaranthus spinosus and Eclipta prostrata were most competitive to upland rice. Echinochloa crusgalli was surprisingly absent

 $\sim 10^{-1}$ km s $^{-1}$

a) Stand reduction and growth reduction were rated at 35 DAS

 $\bar{\beta}$

b)Weed control rating: $10 = \text{excellent}, 0 = \text{no control}$

TABLE 35. POPULATION RATING OF WEED SPECIES FOUND IN UPLAND RICE UNDER DIFFERENT RATES OF APPLICATION OF AMIBEN, CP 53619, RP 17623 AND 2,4-D IPE

a)Weed Population Rating: $5 =$ very high density

 $4 = high$

 $3 =$ moderately high

 $2 = 1$ ow density

 $1 = \text{very}$ low

 $0 = none$

..... \0 \0

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in most plots. Amiben was highly effective in controlling all these weeds at 4.48 kg/ha. Excellent control with amiben was also obtained by Vega and Paller (1967) at 4 kg/ha in corn. Lower rates were less effective. CP 53619 was also most effective at 4.94 kg/ha although at 3.36 kg/ha it was generally satisfactory. It is significant to note that higher rates of herbicides were needed to control weeds in upland soil than in lowland soil due probably to greater intensity of weed infestation and the absence of flooding in upland soil.

RP 17623 was an excellent preemergence herbicide for upland rice even at 2.24 kg/ha. The only disadvantage of using this herbicide was the resistance of Eclipta prostrata to RP 17623 even at 4.48 kg/ha. Anon. (1972) also reported similar result. This species is very common in poorly drained upland soils. Hence, the continuous use of RP 17623 in upland soil in Wai1ua may intensify the build up of Eclipta prostrata.

2,4-D IPE had a short residual effect (about 4 weeks). The weeds quickly took over the bare soil at 6 weeks after sowing. At harvest the plots treated with 2,4-D IPE were as weedy as the unweeded control.

Although the experiment was fully protected from bird damage by netting, the upland rice did not produce any grain yield because IR8 was highly susceptible to cold temperatures in winter. Time of flowering was delayed by a month and 90% of the florets were empty as a result of the cold temperature. Both temperature and daylength actually affect the flowering and growth duration of IR8 (IRRI, 1971). Winter of 1972 was exceptionally cold and wet, and even seedlings planted in January 1972 in the rice nursery of the Paddy-Crop Experiment

Station suffered from high sterility. The panicles were not fully developed and the plant height was relatively short compared to rice grown at higher temperatures. These data suggest that upland rice which is generally grown in wet season and seldom irrigated, does not have a bright prospect in Kauai since the wet season coincides with winter months.

Thus, only yield components and dry matter production can be presented in Table 36. After 5 1/2 months in the field the rice plants became very vegetative, and the annual weeds were dead and dry. This may explain why dry matter yields of rice treated with the three rates of amiben, CP 53619 and RP 17623 were not significantly different from the weeded control, and their weed weights were also relatively low. The dry matter yields of rice treated with 2,4-D IPE were significantly lower than the unweeded control due to both high toxicity and heavy weed infestation. The grain yield of each treatment can be estimated from either the number of panicles per square meter or grain straw ratio. Of the eleven yield components studied, panicle number gave the largest estimate of grain yield $(P = 0.9468)$ (IRRI, 1968). Grain straw ratio, however, varied with climatic factors and soil fertility. In the Philippines the average grain straw ratio of IR8 was 1.0 in dry season and 0.9 in the wet season (IRRI, 1968).

SUMMARY AND CONCLUSIONS

The problem of herbicide toxicity to upland rice was studied using the four preemergent herbicides used in previous lowland rice experiments plus atrazine and diphenamid.

TABLE 36. SOME YIELD COMPONENTS, DRY MATTER PRODUCTION, AND WEED WEIGHT OF UPIAND RICE UNDER DIFFERENT RATES OF AMIBEN, CP 53619, RP 17623 AND 2,4-D IPE

0 N

Activated carbon coating and band application of activated carbon slurry were ineffective in reducing the toxicity of amiben, atrazine and diphenamid. For absolute protection, 2.5 em layer of activated carbon and vermiculite mixture placed over the rice seeds was effective even against highly lethal herbicides such as atrazine, but this method would not be economic.

Deep sowing was adequate in protecting rice seeds from herbicides which were found toxic to flooded directseeded rice. *rae* toxicity of amiben, CP 53619 and RP 17623 was greatly reduced by sowing rice seeds at 3 to 4.5 cm deep compared to shallow seeding of 1.5 cm. Deeper sowing than 4.5 cm resulted in poor seedling emergence.

The response of upland rice and weeds to various rates of amiben, CP 53619, RP 17623 and 2,4-D IPE was studied in the field. Although grain yields were not obtained due to cold temperatures, the toxicity and weed control data indicated that CP 53619 and RP 17623 were highly selective in upland rice even at three times the normal rates used in flooded soil. The lack of toxicity of these herbicides was explained in terms of high adsorption on soil, proximity of the herbicides to rice seed and dilution effects. Amiben and 2,4-D IPE were highly toxic to upland rice presumably due to leaching and high sensitivity of rice to these two herbicides. All the herbicides except 2,4-D IPE effectively controlled most of the weeds in upland soil, especially at high rates.

CHAPTER IX.. THE IMPORTANCE OF HERBICIDE PROPERTIES IN SEED PELLETING

Linscott and Hagins (1967), Bovey and Miller (1969) and others have acknowledged the fact that activated carbon cannot be expected to protect a crop from all types of herbicides. Various experiments conducted with carbon-pelleted seed also indicated that their performance varied with the types of herbicides used. It appears that the use of adsorbents in obtaining herbicide selectivity is dependent on the herbicide properties although these properties have as yet to be defined.

The survival and growth of adsorbent-coated rice seed is dependent on the degree of toxicity of herbicides which in turn is dependent on the amount of herbicide available to rice seed and/or seedlings, accessibility of the available herbicides to the site of uptake, and the sensitivity of rice seed/seedlings to the given herbicides. For these reasons, adsorbability of herbicides by adsorbents and soils, site of uptake, leaching property, the rate of herbicide diffusion to rice seed and inherent susceptibility of rice seed/seedlings to herbicides are all important in determining the survival and growth of adsorbent-coated seed. These herbicide properties were studied here using amiben, CP 53619, RP 17623, 2,4-D IPE and atrazine whenever possible. The results of this study hopefully will give us some basis for explaining the success and failure of adsorbent-coated seed under different herbicide treatments.

MATERIALS AND METHODS

Exp. 1. Inherent susceptibility of rice to herbicides. The objective of this study was to determine the age at which rice seedlings became "resistant" to soil-applied herbicides. Different ages of rice seedlings were planted in one-gallon cans at the rate of 5 hills per can. At the time of herbicide applications the age of seedlings were 0, 3, 10, 17 and 24 days old. Amiben, CP 53619 and atrazine were applied at the rate of 2.24, 1.65 and 2.24 kg per ha, respectively. The herbicides were applied to the soil around the base of the seedlings at the rate of 10 ml per can. A day after the application, the soil was flooded to a depth of 3 em. The treatments were replicated three times. The seedlings were harvested 30 days after the herbicide application.

Exp. 2. Site of uptake. Dawson (1963), Appleby and Furtick (1965), Knake, al. (1967), Parker (1966), Eshel and Prendeville (1967), and Gray and Weierich (1969) have developed different methods for studying the site of entry of herbicides in young seedlings. The Gray and Weierich method was adopted here because of its simplicity and accessibility to activated carbon. To be effective, however, this method required high rates of herbicide application since some was adsorbed by activated carbon present between root zone and shoot zone.

The detailed procedure of the Gray and Weierich method was as follows:

Technical grade amiben, CP 53619, RP 17623 and 2,4-D IPE were dissolved in 95 percent ethanol. Each herbicide was mixed with finely

ground Hauula paddy soil (mesh size: 10) in a 5-gallon mixer for about 10 minutes. The rates of application were 10, 20, 20 and 5 ppmw for amiben, CP 53619, RP 17623 and 2,4-D IPE, respectively. The treated soil was then left overnight to allow the ethanol to evaporate.

For shoot exposure, the bottom portion of a small plastic pot (inside dimensions 10 by 10 cm and 7.5 cm deep) was filled with untreated moist soil to a depth of 3 em. After levelling the soil, a mixture of 50 percent powdered activated carbon Darco G-60 and 50 percent moist vermiculite was added to a depth of 0.5 cm. Rice seed was planted in this layer at the rate of 2 seeds per hill. There were ⁵ hills per pot. ^A little more charcoal-vermiculite mixture was added to just cover the seeds. Finally, a 3-cm layer (equivalent to 450 g) of moist herbicide-treated soil was placed on top of the charcoal layer and subsequently levelled. The charcoal layer prevented the movement of herbicide from the shoot zone to root zone.

For root exposure, the above procedure was repeated except the bottom 3-cm layer was treated with herbicide while the top 3-em layer of soil was not treated.

To expose both the roots and the shoots, the top and bottom layers of the soil were both treated with a herbicide. The charcoalvermiculite mixture was placed in the middle I-em layer of untreated soil to prevent direct exposure of the seeds to herbicide. The rice seed was planted in this charcoal-vermiculite layer.

After treatments, the pots were kept in the greenhouse for 4 weeks. They were irrigated lightly to prevent leaching. Rice seedlings were thinned to four plants per pot after emergence. At the end of 4 weeks, the rice seedlings were harvested to determine the weights of shoots and roots from each pot. Each treatment was replicated three times.

Exp. 3. Leaching Studies. The leaching procedure used in this study was adapted from the method developed by Harris (1966, 1967, 1969). His method differed from the conventional leaching system in that upward movement of water from a free water supply was used to obtain herbicide movement. In the conventional leaching systems, the soil pores tend to plug with fine soil particles which are swept along by gravitational water, and herbicide losses from the top of the columns could also occur through volatilization. None of these disadvantages were found in the Harris method.

Columns were made from I-inch (2.5 em) segments of 7.5 em (inside diameter) ABS (acrylonitrile-butadiene-styrene) tubing with a wall thickness of 2 mm. Lanolin and electric tape were used to waterproof the joints between segments. Air dry Hauula paddy soil was packed uniformly to a depth of 4 cm in the column. The herbicides in 10 ml of 95 percent ethanol were then applied at this level. The treated surface was left overnight to allow the ethanol to evaporate. Amiben, CP 53619, RP 17623 and 2,4-D IPE were used. The rates of application were 3.36 kg/ha except 2,4-D IPE which was l.12 kg/ha.

The columns were completed by packing additional air dry soil to a depth of 5 inches (12.5 cm). The completed columns were set up in a 2.5 liter plastic container so that they could be subirrigated. After adding water to the containers, the units were placed in a hood with the fan operating. After 3 days, the columns were sliced and 10 barnyard grass (Echinochloa crusgalli) seeds were planted per segment. The segments were fertilized and irrigated adequately. After emerging, the barnyard grass seedlings were thinned to five per segment. Fresh weights of barnyard grass were determined after four weeks. The relative mobility factor for each herbicide was computed as described by Harris (1967).

Exp. 4. Adsorption Studies. Initially adsorption studies were carried out using a bioassay procedure developed by Parker (1966) and Coffey and Warren (1969), but this method was time consuming and did not work well with RP 17623. An analytical procedure involving the use of a UV spectrophotometer was finally adopted to study the adsorbability of amiben, 2,4-D, CP 53619 and RP 17623 by three activated carbons, two exchange resins and two soils.

a. Bioassay Procedure (Coffey and Warren, 1969)

A range of herbicide concentrations that would give 50 percent reduction of root growth was prepared by dissolving the technical grade herbicides in distilled water. Exactly 20 m1 of each herbicide solution was added into a paper cup containing 125 g silica sand (standard grade). The herbicide and the sand were mixed by pressing the top of the cup firmly against the bottom of a disposable petri dish and shaking the cup.

After thorough mixing the moist sand was emptied into the bottom portion of the petri dish (diameter: 100 mm, thickness: 15 mm) and smoothed down with the lid so that it was just flush with the rim. Six seeds of sorghum (Sorghum yulgare, Pride 550 hybrid), cucumber (Cucumis sativus, var. poinsett) or rice (Oryza sativa, var. IR8) with their radicles just emerging were placed in a row across the surface of the media with their embryos upward and radicles all aligned in one direction. After placement of seed, the lid was taped firmly on the dish with 2.5 em masking tape in order to prevent evaporation and volatilization of the herbicide solution. The petri dishes were then mounted in a frame at a 75 degree angle so that the roots tended to grow down against the transparent lid. The seedlings were incubated for 48 hr (for sorghum) to 72 hr (for cucumber and rice) in the dark growth chamber at 25 C. The root length was measured at the end of this period to determine I_{50} (50 percent reduction of root growth) in the presence of herbicide only.

The above procedure was repeated in order to determine I_{50} of root growth in the presence of both herbicide and adsorbent. For this purpose 25 mg activated carbon Darco G-60, anion exchange resin or cation exchange resin were added to 20 ml of herbicide solution. The herbicide and the adsorbent suspension were shaken on a Burrell wrist action-shaker for 30 minutes.

Relative adsorption of herbicide was determined as follows:

Relative adsorption = $\frac{I}{I_{50}}$ with adsorbent
 $\frac{I_{50}}{I_{50}}$ without adsorbent

b. Analytical Method

The ultraviolet spectrophotometer has been used frequently recently to determine herbicide adsorption (Müller, 1970; Jordan and Smith, 1971; Hance, 1967; Yamane and Green, 1972; Ward and Getzen, 1969). The procedure is less complicated than adsorption analysis on an automatic liquid scintillation counter although the instrument is less sensitive to small changes in herbicide concentrations.

However, accurate results with the UV spectrophotometer can be obtained if some precautions are strictly observed. Firstly, typical wavelengths of maximum absorption of aromatic compounds lie between 260 and 300 nm. Most herbicides normally give at least two distinct optimum wavelengths, one in the region of 200 to 240 nm and the other in the region of 260 to 300 nm. Optimum wavelength in the region of ²⁶⁰ to ³⁰⁰ nm should always be selected because it is not only unique to that compound, but also less interference is encountered in this region. The response curve of aromatic compounds in the region of 200 to 240 nm was found to be curvilinear, rather than linear. In the region of ²⁶⁰ to ³⁰⁰ nm it was linear, and its magnitude was unaffected by pH of the solution and the type of solvents used.

The second precaution is the choice of solvent. The best solvent is freshly prepared distilled water. Both pure methanol and ethanol were found to be poor solvents since the blank solutions made from these solvents had absorbance readings much greater than 0.5 when they were checked against air. The maximum permissible readings for

blank solutions are 0.5. Higher readings will cause erroneous readings of the unknown due to the high amount of stray light. $*$ These errors can be minimized by dissolving the water-insoluble herbicides in 25 or 50 percent alcohol. The less alcohol in the solvent, the less interference will be encountered, especially in dealing with soils of high organic matter content.

The last precaution is the necessity of preparing a blank for every solvent and adsorbent used since the absorbance of the blank is affected by the nature of adsorbent and solvent, and by the length of time they are shaken.

The adsorption procedures adopted in this study were as follows:

The optimum wavelengths of amiben, CP 53619, RP 17623 and 2,4-D acid (2,4-D IPE was substituted by 2,4-D acid since pure 2,4-D IPE sample was not available at the time of analysis) were first determined on a Unicam SP1800 ultraviolet spectrophotometer. Amiben and 2,4-D were dissolved in distilled water while CP 53619 and RP 17623 were dissolved in 50 percent methanol. The wavelengths at which maximum absorption occurred were 298, 266, 292 and 283 nm for amiben. CP 53619, RP 17623 and 2,4-D, respectively. A standard curve for each of these herbicides was established at these wavelengths. The adsorbability of the adsorbents and soils was determined by measuring the concentration of a standard aqueous solution before and after equilibrium with a given amount of the adsorbent or soil. The difference between the

^{*}Straylight is radiation whose wavelengths are outside a given bandwidth, usually widely distributed. Because of the stray multiplication effect, spurious maxima may be observed even away from the ends of the wavelength range, where the amount of straylight would otherwise be quite small.

final and initial readings was assumed to represent the amount of herbicide adsorbed by the adsorbent or soil.

The adsorbability of five adsorbents and two soils were evaluated for their comparative efficiency in adsorbing amiben, CP 53619, RP 17623 and 2,4-D from aqueous solution. The physical and chemical properties of the adsorbents and the soils are presented in Table 37. Ten to 100 mg of adsorbent or 1 to 2 gm of soil and 20 ml of the herbicide solution were placed in a 75-ml centrifuge tube and shaken on a Burrell wrist-action shaker for 3 hr, the optimum period of equilibration found to obtain maximum adsorption. Just before shaking, the pH of herbicide $+$ exchange resin solution was adjusted with 0.01 M KOH to approach the pH of the soil plus herbicide, since the adsorbability of exchange resins is dependent on pH (Ward and Getzen, 1970). After shaking the tubes were centrifuged at 12,000 rpm for 20 minutes, and the supernatants were either filtered through a Whatman No. 42 filter paper or pippetted out for analysis. Three concentrations for each adsorbent were run in three replications and the experiments were repeated, if required.

Adsorption isotherms for each herbicide were then plotted and adsorption efficiency (Kd) was calculated as follows:

> Kd = amount adsorbed amount in equilibrium solution

$$
= \underline{\text{ppm standard - ppm in equilib. solution}} \times \underline{\text{ml of solution}} \times \underline{\text{gm of adsorbent}}
$$

TABLE 37. PHYSICAL AND CHEMICAL PROPERTIES OF ADSORBENTS AND SOILS

 $a)$ 1:4 ratio for activated carbons and exchange resins, and 1:1 ratio for soils

The relationship between adsorption of solutes at liquid-solid interfaces is often described mathematically using the empirical Freundlich equation (Freundlich, 1926) which is as follows:

$$
x/m = kc^{1/n}
$$

where $x/m =$ amount of solute (x) adsorbed by a given amount of adsorbent (m),

c = concentration of solute in solution at equilibrium, k and $n =$ constants.

The logarithmic expression of this equation is log $x/m = log$ k+ *lin* log c. A plot of log x/m vs log c gives a straight line of slope *lin* and intercept of log k. Grover (1971), Hance (1965) and Harris (1966) reported that their data exhibited ^a good fit to this relationship over a wide range of concentrations of different herbicides.

Exp. 5. Herbicide diffusion to rice seed. Diffusion of amiben, CP 53619, RP 17623 and 2,4-D to both uncoated and triple carboncoated rice seed was also studied. Herbicide concentrations were measured on a Unicam SP1800 ultraviolet spectrophotometer. Because this instrument was not very sensitive to small changes in herbicide concentrations, high concentrations of herbicides (40 ppm for uncoated seed and 80 ppm for carbon-coated seed) were used in most of the determinations. Herbicide uptake over 48 hr at 30 C was directly proportional to the concentration of the soaking solution (Rieder, al., 1970), hence larger changes in herbicide concentrations would occur at high concentrations than at low concentrations over a period of time.

Three lots of ten presoaked seeds of uniform size were placed in 20 ml of solution containing a known concentration of the herbicides. The seeds were either soaked in water (for amiben and 2,4-D determinations) or in 50 percent methanol (for CP 53619 and RP 17623 determination) for 12 hours. Maximum inhibition of seed was achieved in 8 hr with soybean (Rieder, et al., 1970). At the end of 12, 24, 36 and 48 hr the rice seeds were removed. The difference in concentration of the solution at the beginning and end of each time period gave a quantitative measure of the uptake of the four herbicide by the seeds. The air dry weight of each lot was determined before placing the seed in the solution.

Similar procedure was adopted for studying the uptake of herbicides by carbon-coated rice seed. The seed was coated with activated carbon Darco G-60 three times with 50 percent polyvinyl acetate. The mean weight of carbon coating per seed was 9.8 mg.

Since it is difficult to evaluate the amount of herbicide adsorbed by carbon coating unless water uptake by the seed is prevented completely, another lot of seed was first pel1eted with polyvinyl chloride (PVC) before coating the seed with activated carbon. Polyvinyl chloride was sprayed on the seeds several times until they were fully coated. Uptake of water was completely blocked by PVC coating but the resultant seeds had irregular shape. These seeds were coated with activated carbon three times in the usual manner, but the weight of coating per seed was found to be very heavy (about 14.6 mg).

Exp. 6. The extent of adsorbed area around the carbon-coated rice seed. Since carbon-coated rice seed germinated and survived in soil treated with toxic chemicals while the ordinary rice seed dies, it was deemed necessary to determine the extent of adsorbed area around the coated seed. The degree of protection against herbicide toxicity which the coating affords hopefully can be correlated to the size of this area. This determination, however, could not be carried out using an autoradiographic technique, since clear-cut black and white pictures will be obtained only if the area in question is completely freed from herbicide by activated carbon (personal communication with Dr. T. L. Lavy). Since it was doubtful that activated carbon weighing only ¹⁰ to ¹⁵ mg could adsorb all the herbicide present around the seed at the rate it is used in the field, a bio-assay technique was developed to determine the adsorbed area.

For this bio-assay barnyardgrass seed was selected since its seed is very small (only 2 mm thick) and the plant can grow even in poorly drained soil, such as the lowland soil used in these experiments. The procedure was as follows:

Rice seeds were coated with activated carbon three times in the usual manner. They were then planted on pots containing puddled soil in five rows, four seeds per row. Each row was bioassayed every day starting a day after the application of 2.24 kg/ha amiben, 1.65 kg/ha CP 53619, 3.36 kg/ha RP 17623 and 0.90 kg/ha 2,4-D IPE. Barnyardgrass seed was then sown on both sides of the slender rice seed to a depth of five barnyardgrass seed. Since the thickness of the barnyardgrass

seed was 2 mm, 5 seed would represent a distance of 10 mm away from the coated rice seed. Each treatment was replicated four times. At the end of 3 weeks the nmnber of seedling survival and percentage growth reduction was determined from each treatment. The nmnber of seedling surviving and percentage of growth reduction of barnyardgrass were assmned to be correlated to the size of adsorbed area around the carbon-coated rice seed.

RESULTS AND DISCUSSION

Experiment 1

Figure 23 shows that rice seedlings gained some resistance to the preemergence herbicides, CP 53619 and amiben, with increasing age, but seedlings treated with CP 53619 appeared to recover completely at least 14 days earlier than the seedlings treated with amiben. Seedlings treated with amiben showed some injury even with 24-day-old seedlings, but the degree of toxicity was markedly reduced with age of the seedlings as could be seen with their plant height and tillering capacity compared to the untreated control. The CP 53619 treated seedlings, on the other hand, showed slight injury when they were ten days old. The l7-day-old seedlings appeared to be completely resistant to this herbicide.

Atrazine was found to be lethal to rice seedlings of all ages. The seedlings appeared healthy during the first 10 days after treatment. After that the leaves gradually became chlorotic and finally died. At the time of sampling all the treated seedlings except the 24-day-old seedlings were dead. The latter seedlings were still standing

although 75% of the leaves were already dead. Given another week or two these seedlings would have died too. The susceptibility of rice to atrazine was to be expected since attempts to develop it for transplanted rice have never been successful, presumably because rice cannot detoxify it to hydroxy analogue as in corn. All other cereal crops are resistant to atrazine (Hepworth and Fine, 1971).

Response of different ages of rice seedlings to soil-applied 2,4-D IPE and high application rates of RP 17623 was not studied. But data obtained by De Datta, Lacsina and Seaman (1971) seem to indicate that 2,4-D IPE behaves somewhat like amiben although it is probably more toxic. They noted, however, that ester formulations of 2,4-D was less toxic than salt formulations of 2,4-D.

Experiment 2

The growth of rice was more severely inhibited by root-applied amiben than by shoot-applied amiben (Figure 24). This result was in agreement with Knake and Wax (1968) and Linscott, et al. (1969). The other herbicides, CP 53619, RP 17623 and 2,4-D IPE caused a greater reduction in fresh weights of shoot and root when they were placed in the shoot zone than in the root zone. Results on RP 17623 were in agreement with the published data of Rhodia company (Anon. 1972). Prendevi11e, et al. (1967), however, reported that the site of uptake of 2,4-D amine in corn and pea was primarily in the root region. 2,4-D IPE reduced fresh weights of rice considerably when the roots were exposed to it, but fresh weight reduction was smaller than when it was exposed in the shoot zone. Site of uptake of ^a herbicide seems to be affected by the type of species, for Knake and Wax (1968)

COMPARISON OF SHOOT, ROOT AND SHOOT + ROOT EXPOSURES OF RICE TO AMIBEN, CP 53619, RP 17623, AND 2,4-D IPE AS MEASURED BY THE RESPONSE OF SHOOTS AND ROOTS FIGURE 24.

reported that the site of uptake of 2,4-D in green foxtail (Setaria viridis L.) was in the shoot region.

Exposure of both roots and shoots to all the four herbicides inhibited growth more than either single application but significant differences in both fresh weights of root and shoot were only observed with 2,4-D IPE (Figure 24). Nishimoto and Warren (1971) also observed a similar trend when both shoot and root of sorghum (Sorghum bicolor L.) were exposed to DCPA.

Experiment 3

Amiben was extremely mobile in Hauula paddy soil as indicated by the large reduction in fresh weights of barnyardgrass in the upper two 2.5 em segments (Figure 25). CP 53619 remained predominantly in the lower two 2.5 em segments while RP 17623 hardly moved beyond the first 2.5 em segment. The mobility of 2,4-D IPE was intermediate in that most of it remained in the first three 2.5 em segments. Mobility factors for amiben, 2,4-D IPE, CP 53619 and RP 17623 in soil columns were 3.69, 2.13, 1.30 and 1.09, respectively. Harris (1967) obtained a greater mobility factor for amiben (5.2) in Hagerstown silty clay loam which contained 4.3% organic matter and 30% clay. The larger mobility factor obtained by Harris in this soil could be attributed to differences in soil texture. Although the relationship between adsorption and movement is not fully understood, it is well accepted that herbicides are leached to a greater degree in lighttextured soils than in heavier-textured soils (Ogle and Warren, 1956; Harris, 1964; Donaldson and Foy, 1965; Kearney, et al., 1965).

FRESH WEIGHT AS % OF CONTROL

FIGURE 25. MOVEMENT OF HERBICIDES IN SUBIRRlGATED HAUUIA PADDY SOIL AS SHOWN BY FRESH WEIGHTS OF BARNYARDGRASS IN I-INCH (2.5 CM) SEGMENTS

The low mobility factors of CP 53619 and RP 17623 were probably due to high adsorption of these compounds by Hauula paddy soil and their insolubility in water. Darlington, Briner, and Sutherland (1971) reported that only 2.6 to 3.5 percent of applied butachlor or CP 53619 was found in the first leachate that was passed through in a 5 cm soil. Both run-off and leaching data indicated that the l4C of butach10r became less mobile with time.

Experiment 4

Comparisons of amiben 2,4-D, CP 53619 and RP 17623 adsorption on three types of activated carbon, two exchange resins, and two soils are presented in Figures 26, 27, 28, and 29. In all cases, the four herbicides were highly adsorbed by activated carbons. The degree of adsorption, however, varied with the types of carbons. Herbicide adsorption on Witco 249 consistently exceeded that on Norit A which in turn exceeded that on Darco G-60. These results confirmed the findings of Jordan and Smith (1971) on atrazine and diuron adsorption on these three activated carbons. The high adsorption capacity of Witco 249 relative to Norit A and Darco G-60 cannot be explained in terms of surface area and pH, since the surface area of Witco 249 was the smallest and its pH was intermediate compared to the other two carbons, The intensity of adsorption, as measured by the slope of the log-log plot of x/m vs C, however, differs among the three carbons. Although the adsorption capacity of Darco G-60 was the smallest, its adsorption intensity was the highest among the three carbons, except in the case of RP 17623 adsorption (Figures 26 and 27). The adsorption of RP 17623 on Darco G-60 was inefficient in terms of both adsorption capacity and

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FIGURE 26. ADSORPTION ISOTHERMS OF AMIBEN AND 2,4-D ON THREE TYPES OF ACTIVATED CARBONS AND ANION EXCHANGE RESIN

FIGURE 27. ADSORPTION ISOTHERMS OF CP 53619 AND RP 17623 ON THREE TYPES OF ACTIVATED CARBONS

FIGURE 28. ADSORPTION ISOTHERMS OF AMIBEN AND 2,4-D ON CATION EXCHANGE RESIN AND TWO SOILS

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 $\sim 10^{11}$ km s $^{-1}$

 $\mathcal{O}(n)$ and the second construction of the following function $\mathcal{O}(n)$ and $\mathcal{O}(n)$, $\mathcal{O}(n)$, $\mathcal{O}(n)$, $\mathcal{O}(n)$

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FIGURE 29. ADSORPTION ISOTHERMS OF CP 53619 AND RP 17623 ON TWO EXCHANGE RESINS AND TWO SOILS

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adsorption intensity. These factors may explain why triple carboncoated rice seed was not very effective in protecting rice from high rates of application of RP 17623, although the herbicide was highly adsorbed by soil and insoluble in water.

Amiben and 2,4-D adsorption far exceeded CP 53619 and RP 17623 adsorption on anion exchange resin (Figures 26 and 29). At pH 6, which was used in this analysis, ionization of aromatic carboxylic acids including amiben and 2,4-D was nearly complete, i.e. about 99 percent of the compounds was present in the ionic form and the remaining 1 percent in the molecular form (Ward and Getzen, 1970). The pKa values of amiben and 2,4-D were 3.4 and 3.3, respectively (Ward and Getzen, 1970). The high adsorption of amiben and 2,4-D on anion exchange resin can be attributed to the high ionization of these herbicides in solution. CP 53619 and RP 17623 probably existed primarily in molecular form. The adsorption of amiben and 2,4-D on anion exchange resin exceeded that on activated carbons, although the difference was not very large. The bioassay data presented in Table 38 and those obtained by Coffey and Warren (1969) on amiben and 2,4-D showed a reverse trend with respect to the adsorption of these compounds on Darco G-60 and anion exchange resins. The discrepancy can be attributed to the desorption of some of the herbicides during the three day incubation since the adsorbents were not separated out during the analysis, or to the differences in the pH of the solutions. The unadjusted pH of the anion exchange resin in amiben or 2,4-D solutions was about 4.3.

| Herbicide Adsorbent | | I_{50} ^{a)} | in PPM | Relative Adsorption ^b) |
|---------------------|----------------------|------------------------|---------|---------------------------------------|
| | | With | Without | |
| Amiben | Darco G-60 | 6.40 | 0.88 | 7.27 |
| | Anion exchange resin | 4.80 | 0.88 | 5.45 |
| | Cation exch. resin | 0.90 | 0.88 | 1.02 |
| CP 53619 | Darco G-60 | 94.00 | 4.35 | 21.61 |
| | Anion exch. resin | 5.80 | 4.35 | 1.33 |
| | Cation exch. resin | 9.80 | 4.35 | 2.27 |
| $2,4-D$ IPE | Darco G-60 | 10.23 | 0.31 | 33,00 |
| | Anion exch. resin | 0.68 | 0.31 | 2.13 |
| | Cation exch. resin | 0.42 | 0.31 | 1.35 |

TABLE 38. I_{50} VALUES OF AMIBEN, CP 53619 AND 2,4-D IPE WITH AND WITHOUT ADSORBENTS

a) I_{50} = concentration of herbicide sclutions added to give
50% root inhibition of the test plant

b) Relative adsorption = $\frac{I_{50}}{I_{50}}$ with adsorbent
 I_{50} without adsorbent

Comparisons of 2,4-D IPE and 2,4-D acid adsorption on anion exchange resin are shown in Table 38 and Figure 26. 2,4-D adsorption exceeded 2,4-D IPE suggesting that adsorption of 2,4-D on anion exchange resin was dependent on water solubility and the ability of the herbicides to ionize in solution.

Amiben and 2,4-D were poorly adsorbed by cation exchange resin indicating that these herbicides existed primarily as an anion. However, the adsorption of CP 53619 and RP 17623 on cation exchange resin was nearly six times greater than anion exchange resin (Figure 29). The surface areas of the two resins were nearly the same, hence the differences in adsorption capacity of the two exchange resins can be attributed to the large exchange capacity of cation exchange resin relative to that of anion exchange resin (Table 37). The importance of exchange capacity in herbicide adsorption has been reported by some workers (Sheets, et al., 1962; Upchurch and Mason; Yamane and Green, 1972).

Amiben was poorly adsorbed by both Wailua and Hanalei soil (Figure 28). The result was in agreement with Talbert, et al. (1970) and Linscott, et al. (1969). The adsorption of the four herbicides on Wailua soil was generally greater than that on Hanalei soil as was expected, since the former soil contained nearly twice as much organic matter as the latter soil (Figures 28 and 29). Herbicide adsorption was strongly correlated to organic matter content of the soil (Upchurch and Mason, 1962; Sheets, et al., 1962; Grover, 1965; Harris and Sheets, 1965; Obien, et al., 1966; Day, et al., 1968, Liu, et al., 1970; Yamane and Green, 1972).

The adsorption coefficients (Kd) of the five adsorbents and the two soils are summarized in Table 39, Although activated carbon is thought to have large capacity to adsorb undissociated molecules (Anderson, 1947), the results indicated that adsorption coefficients of amiben and 2,4-D on the three activated carbons generally exceed those of CP 53619 and RP 17623. With other adsorbents and soils there was also no apparent correlation between water solubility and adsorbabi1ity among the four herbicides. According to Bailey and White (1970) the relationship between solubility and adsorbabi1ity exists only in the same chemical family but not within different types of herbicides. Furthermore, the four herbicides were analyzed in different solvents which make it difficult to make valid comparisons. Within the same solvent, adsorption of RP 17623 on adsorbents and soils was generally greater than that of CP 53619, probably because the former herbicide was less soluble in water. Between amiben and 2,4-D, activated carbons and anion exchange resins adsorbed amiben to a larger degree than 2,4-D, but the two soils adsorbed more 2,4-D than amiben.

Experiment 5

The amount of herbicides absorbed by rice seeds generally increased with time even though they were presoaked in water or 50 percent methanol before the experiment was started, suggesting that herbicide uptake was indeed independent of water uptake as also found by Rieder, et al. (1970) and Scott and Phillips (1971). The rates of absorption, however, varied with the type of herbicide used (Figure 30). After 48 hr 30% of the 2,4-D, 23% of the amiben, 18% of

TABLE 39. ADSORPTION COEFFICIENTS (Kd) OF AMIBEN, 2,4-D, CP 53619 AND RP 17623 ON FIVE ADSORBENTS AND TWO SOILS AND THE pH AT WHICH THE VALUES WERE OBTAINED (AVERAGE OF 3 CONCENTRATIONS AND 3 REPLICATIONS)

FIGURE 30. UPTAKE OF AMIBEN, CP 53619, RP 17623 AND 2,4-D BY
UNCOATED AND TRIPLE CARBON-COATED RICE SEED

the CP 53619, and 10% of the RP 17623 in the original solution had been absorbed by the seed. The initial absorptions of CP 53619 and RP 17623 were extremely slow in that they could hardly be detected during the first 12 hours.

The absorption of the four herbicides by carbon-coated rice seed exhibited a similar pattern as that of uncoated rice seed (Figure 30). The only exception was that the uptake of amiben and 2,4-D by the carbon-coated seed was very rapid during the first 24 hr, thereafter the rate of uptake tended to level off. Such a trend was not observed with CP 53619 and RP 17623. The uptake of these two herbicides by the coated seed was slow but steady. On the average, total uptake of the four herbicides by the carbon-coated seed was increased by' ten fold compared to that by uncoated seed.

None of the four herbicides showed high rates of diffusion as found by Rieder, et al. (1970) with EPTC and chlorpropham. According to Scott and Phillips (1971) the absorption of herbicides by seed was influenced by solubility of the herbicide in the soil solution, diffusion rate of the herbicide in the seed and/or soil, oil and protein content of the seed, hardness or nature of the seed coat, size and shape of the seed, soil water content, soil temperature, and chemical structure of the herbicide. But Rieder, et al. (1970) attributed the high absorption rates of chloropropham and EPTC relative to amiben and atrazine in soybean seed to higher solubility of the former herbicides in lipids. Thus, chlorpropham and EPTC may have moved through the seed coats and internal cell membranes more readily and been absorbed preferentially in the seed lipids reserves.

Data on the solubility of CP 53619 and RP 17623 in lipids are not available, but they are much less soluble in water than amiben and 2,4-D. Differences in water solubility may account for the slow absorption of CP 53619 and RP 17623 by rice seed compared to 2,4-D and amiben, although these data are not conclusive because of the differences in the solvents used in the determinations.

In Table 40 adsorption efficiency of activated carbon (Darco G-60) coating was computed by assuming that all the herbicides absorbed by carbon-coated seed was adsorbed by the carbon and none was passed through this carbon layer into the seed. This assumption is valid since **--** as we will see later **--** the adsorption coefficients of this coating was far below its maximum potentials. By comparing the adsorption coefficients of carbon-coated seed after 48 hr equilibrium with herbicide solutions with the adsorption coefficients obtained by shaking 10 to 25 mg carbon in 20 ml herbicide solutions in 3 hr, it was found that efficiency of carbon coating in adsorbing herbicides ranged from as low as 4.4% to high as 25.7%, an average of 13.3 percent for the four herbicides. Such a low efficiency can be attributed to two factors: (a) by the large reduction of the surface area of activated carbon exposed to the herbicides, and (b) by the absence of vigorous shaking to achieve maximum adsorption. The efficiency of carbon coatings seemed to be influenced by the rate of herbicide diffusion as well as the weight of carbon coating per seed. The faster the movement of herbicide to rice seed and the greater the weight of carbon per seed, the more efficient the carbon in adsorbing the herbicide around the seed. The higher efficiency of heavy coating compared to light coating can be seen from Table 40 as well. Seed
TABLE 40. ADSORPTION EFFICIENCY OF ACTIVATED CARBON (DARCO G-60) COATING REIATIVE TO MAXIMUM ADSORPTION OBTAINED BY 3 HR SHAKING

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*PVC = polyvinyl chloride, ^a spray solution used prevent the entry of water into rice seed to

initially coated with polyvinyl chloride (PVC) before coating it with activated carbon was heavier than seed not initially coated with PVC due to uneven shape of PVC coating. The weight of carbon per seed was 14.6 mg in PVC-coated seed compared to 9.8 mg in seed not coated with PVC. There was an increase of adsorption efficiency of 5.8% in amiben and 9.0% in 2,4-D as a result of the increase in weight of carbon per seed.

Experiment 6

Results presented in Figure 31 seemed to confirm the findings obtained in adsorption and herbicide diffusion studies. These data showed the number of barnyardgrass seedling survival increased with time after application and then levelled off at about 3 days after herbicide application in all the four herbicides except RP 17623. At the same time the percentage of growth reduction also decreased with time after herbicide application and then levelled off at about 3 days as well. This decrease was probably due to both increased herbicide adsorption by carbon and decreased soil moisture on the soil surface. Herbicide toxicity and effectiveness was known to be influenced by soil moisture (Jordan, et al., 1968; Stickler, et al., 1969). As described earlier the water content of surface puddled soil decreased from about 150% down to about 80% during the first week after sowing. On the first day after application amiben, CP 53619, RP 17623 and 2,4-D were highly lethal to barnyardgrass seeds even though they were located near the carbon-coated rice seed suggesting that weed control activity was not reduced by the presence of large numbers of carbon-coated rice seed on the first and second

FIGURE 31. EXTENT OF ADSORBED AREA AROUND THE TRIPLE CARBON-COATED RICE OVER TIME AFTER HERBICIDE APPLICATION AS SHOWN BY THE NUMBER OF SEEDLING SURVIVAL AND GROWTH REDUCTION OF BARNYARD GRASS SEEDLINGS

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day after herbicide application. The largest increase in seedling survival of barnyardgrass was in 2,4-D IPE treated plots followed by plots treated with amiben, CP 53619 and RP 17623. But these data had to be carefully interpreted in terms of size of adsorbed area because 2,4-D IPE was not very toxic to barnyardgrass, especially under nonflooded conditions (Obien, et al., 1971), whereas RP 17623 was exceptionally toxic to most of the annual weeds including barnyardgrass especially when it was applied three times the normal rate of application as was done in this experiment. Despite this, the data clearly demonstrated that herbicide adsorption and herbicide diffusion by and to the carbon-coated rice seed were time-dependent. Maximum adsorption of herbicides by the carbon-coating was not reached three days after the herbicide application. At these maxima, growth reduction of barnyardgrass still occurred suggesting that not all of the herbicide around the seed was adsorbed by the carbon. In the laboratory, near-complete equilibrium was achieved in 24 hr with amiben and 2,4-D (Figure 31). The data for these two herbicides cannot be compared, since in soil the concentration of herbicide around the seed was in the state of dynamic equilibrium with the rest of the herbicide present in the soil. In the enclosed vials, where the herbicide diffusion in laboratory took place, such a phenomenon did not exist.

SUMMARY AND CONCLUSIONS

Herbicide properties which are considered important in influencing the effectiveness of adsorbent coated rice seed were studied using

amiben, CP 53619, RP 17623 and 2,4-D IPE (or 2,4-D acid), the four most frequently applied herbicides in these pelleting experiments.

Amiben was highly toxic to rice up to 24 days after sowing. It was extremely mobile in Wailua (Hauula paddy) soil as a result of both poor adsorption by soil and high solubility in water. Its primary site of uptake was in the root region. This root activity coupled with high mobility in soil were probably the main contributing factors why it was toxic to both lowland and upland rice. Amiben coxicity, however, did not persist very long, probably because the herbicide was easily washed away by the drainage water.

2,4-D IPE was much more toxic to rice than amiben although it was less mobile in soil. Its primary site of absorption was in the shoot region.

In contrast, CP 53619 was only moderately toxic to rice seed and rice seedlings. Rice was resistant to this herbicide when it was applied 10 to 17 days after sowing. The herbicide was only slightly soluble in water, and highly adsorbed by soils which explain why it was less mobile than either amiben or 2,4-D IPE. Its primary zone of entry was via the shoot.

The properties of RP 17623 in terms of site of uptake and mobility in soil were very much similar to CP 53619. RP 17623 was toxic to directseeded flooded rice only when it was applied at rates greater than 2.24 kg per ha. Atrazine, in contrast, was lethal to rice at any age up to ²⁴ days after sowing. It was known to be highly adsorbed by activated carbon (Jordan and Smith, 1971; McGlamery, 1965), and hence the failure of activated carbon coating in protecting rice from atrazine and other similar types of herbicide can probably be

attributed to inability of rice seedlings to withstand atrazine toxicity with increasing age. Activated carbon coating adsorbed herbicides only around the seed. The remaining herbicide could enter the seedlings through the roots or shoots at later stage when the soil was flooded to a depth of 3 to 5 em.

Both bioassay and analytical data indicated that activated carbon was superior to exchange resins in herbicide adsorption. Exchange resins were effective adsorbents only if the herbicides exist primarily in ionic forms, as in the case of amiben and 2,4-D. The specificity of exchange resins in adsorbing herbicides make them undesirable for use as pelleting materials. An excellent adsorbent should be able to adsorb any kind of herbicide, irrespective of whether they are easily ionized or not, or whether they are very mobile in soil or not.

Among the three activated carbons studied, Witco 249 had a higher adsorption coefficient than either Norit A or Darco G-60. Darco G-60 had the lowest adsorption coefficient, but its adsorption intensity was the highest except in the case of RP 17623. RP 17623 was inefficiently adsorbed by Darco G-60 in terms of adsorption capacity as well as adsorption intensity.

The roles of organic matter content and cation exchange capacity in herbicide adsorption were dramatically demonstrated in these studies.

The diffusion of amiben, CP 53619, RP 17623 and 2,4-D to rice seed was generally very slow. In terms of total uptake in 48 hr, 2,4-D showed the highest rate of diffusion, followed by amiben, CP 53619 and RP 17623. This order was not changed by coating rice

seed with activated carbon Darco G-60 suggesting that herbicide adsorption on activated carbon coating was dictated mainly by the rate of herbicide diffusion. The total uptake of herbicides by carboncoated seed, however, was increased by ten fold. Assuming that none of the herbicides was absorbed by seed itself, the adsorption efficiency of carbon coating was found to be as low as 4.4% with RP 17623 to as high as 25.7% with 2,4-D. Such a low efficiency seriously limits the capability of activated carbon in protecting rice seed from toxic herbicides.

Bioassay data also indicated that herbicide diffusion to carbon-coated seed was time-dependent. Maximum adsorption of herbicides by carbon-coated rice seed occurred about 3 days after herbicide application. This implies that pregerminated coated seeds which normally germinate one day after sowing, cannot be totally prevented from absorbing toxic herbicides through the emerging radicles and/or co1eoptile.

CHAPTER X. GENERAL SUMMARY AND CONCLUSIONS

The difficulty of controlling weeds by hands or mechanical means and the lack of selectivity of many preemergence herbicides to directseeded rice (Oryza sativa L.) prompted this study to determine whether the use of adsorbent pe11eting would be possible and feasible to overcome herbicide phytotoxicity. The principle behind this technique was the reduction of total herbicide available to rice seed through herbicide adsorption on the adsorbent, thus allowing coated or pe11eted rice seed to survive and to grow to maturity. However, such a simple idea was not easily put into practice since herbicide toxicity did not stop at germination stage, but rather it persisted as long as rice was sensitive to it.

Field and greenhouse experiments were conducted at Hawaii Agriculture Experiment Station on Kauai from June 1970 up to May 1972 to develop an effective seed pe11eting procedure and to define factors which would favor or limit its performance. IR8 rice seed was used throughout the study. The effectiveness of adsorbent-pe11eted seed was treated against 3-amino-2,5-dich1orobenzoic acid (amiben), 2-ch1oro-2',6'-diethy1-N(butoxymethy1) acetanilide (CP 53619), 2-tertiary butyl-4-2'-4 ¹ -dich1oro-5'-isopropy1oxypheny1-1,3,4 oxadiazo1ine-5-one (RP 17623), (2,4-dich1orophenoxy)acetic acid isopropyl ester (2,4-D IPE) and a few other preemergence herbicides.

Of the three possible sowing methods normally practiced in directseeded rice, sowing pe11eted seed on puddled, nonf1ooded soil was most likely to succeed for two reasons: (a) intimate contact between herbicide and adsorbent, and (b) the absence of standing water which

might inhibit seedling growth. In separate experiments in flooded soil and upland soil, it was found that weed pelleting did not protect rice when it was sown in water or below the soil surface under upland conditions.

Pelleted seeds did not germinate well when broadcast on nonflooded, puddled soil unless they were pregerminated before coating them with an adsorbent. The cause of this poor germination was (a) rapid loss of water from rice seeds and the soil surface when the puddled soil was drying due to direct exposure of seeds to sunlight, and (b) slow germination of presoaked rice seed. However, the use of pregerminated seeds in seed pelleting had four disadvantages: (a) the necessity of sowing them as soon as they had been pelleted unless they were stored in the shade at 10 to 15 C; (b) reduced total emergence by about 15 percent due to the injury of pregerminated seeds during pelleting in a 5-gallon concrete mixer; (c) early emergence of radicles and coleoptiles in soil (normally one day after sowing) before complete herbicide adsorption on activated carbon was achieved at 3 DAS; and (d) the necessity of synchronizing the processes of land preparation, soaking + incubation of seed, pelleting, sowing and herbicide application so that no delay was made in carrying out one operation to the next. A better sowing method needs to be investigated to obtain high germination on puddled, nonflooded soil with minimum consequences or complications.

Pelleting materials - both the adhesive and the adsorbent - had to be carefully selected since they affected the performance of pelleted seed in puddled soil. The only adhesive which met the

requirements of nontoxicity, pe11eting stability and low viscocity was polyvinyl acetate (PVA) which was used at 50%. The other four adhesives - methyl cellulose, methyl ethyl cellulose, gum arabic and dry casein glue - were either toxic or produced unstable coatings. Of the three adsorbents studied, activated carbon Darco G-60 used alene was better or comparable to cation exchange resin, anion exchange resin, or a combination of *two* or three of the adsorbents in soil treated with amiben. CP 53619 and RP 17623. The failure of exchange resins as pe1leting materials was due to their specific adsorption capacity and the poor quality of coatings made from these adsorbents. The above herbicides were poorly adsorbed by cation and anion exchange resins, except amiben which was highly adsorbed on anion exchange resin.

Besides adsorption capacity, both coating weight and coating quality were extremely important in increasing the degree of protection afforded by the coatings. In the greenhouse, increasing the number of coating layers of activated carbon Darco G-60 greatly improved the performance of coated seed in soil treated with toxic amiben, CP 53619 and RP 17623, possibly due to the increase in adsorption efficiency with heavy coating. In another experiment where rice seeds were coated three times with different types of activated carbons, Darco G-60, Norit A and Witco 249, Norit A consistently performed better than the other two types of carbons, although Witco 249 was found to have the highest adsorption coefficients among the three adsorbents in analytical study conducted on a UV spectrophotometer. The failure of Witco ²⁴⁹ was mainly due to the larger size of its

particles (mesh size 80) which made it difficult to coat it on rice seed. For excellent coatings the mesh size of adsorbent should be at least 200. Coatings made from Darco G-60 were excellent but consistently ineffective in protecting rice seed from RP 17623 partly because RP 17623 was poorly adsorbed on Darco G-60 in terms of adsorption capacity and adsorption intensity.

In the subsequent experiments conducted both in the greenhouse and the field, factors that affected the performance of triple carboncoated rice seed (Darco G-60) in flooded soil were carefully evaluated. The results of these experiments were correlated to findings made in the laboratory with regard to herbicide adsorption on adsorbents and soils, leaching, site of uptake, sensitivity and inherent susceptibility of rice to herbicides, and herbicide diffusion to coated and uncoated seed.

Among the factors which improved the effectiveness of triple carbon-coated rice seed were: (a) delaying the flooding of the soil until rice seedlings had reached 2 - 3 leaf stage, (b) application of water-insoluble herbicides 1 or 2 days before sowing, (c) application of the lowest possible rate of herbicide to obtain high percent seedling survival as well as effective weed control, (d) relatively high seeding $rates$ (100 - 120 kg/ha) but not too high as to cause lodging, and (e) high adsorption capacity and high coating quality of activated carbon.

Triple carbon-coated seed consistently performed better than uncoated rice seed in many of the experiments conducted in the green house and the field as measured by seedling survival per unit area.

Unfortunately, many of these seeds were killed and those that survived showed some injury, although the degree of toxicity was significantly less than that of uncoated seeds. The causes of this mortality and/or injury can be attributed to one or more of the following factors:

a. The limited amount of activated carbon which could be pelleted on rice seed even with triple coatings. Coating weight per seed varied from ⁹ to ¹⁷ mg. Its adsorption efficiency was even reduced further by at least 75 percent due to large reduction of surface area of carbon exposed to the herbicides, compared to that of carbon which remained as fine powder. Adsorption efficiency of carbon coatings appeared to be dependent on rate of herbicide diffusion and coating weight.

b. Herbicide diffusion was time - dependent, and herbicide adsorption on carbon coating was influenced by rate of herbicide diffusion. Bioassay data indicated that maximum herbicide adsorption by carbon coating occurred at least 3 days after herbicide application, which means that the carbon coating was ineffective in stopping the flow of herbicide to emerging radicles and coleoptile, causing severe injury of the emerging seedlings. This problem was intensified if the herbicides were applied two days after sowing or the sprouted coated seeds were broadcast on pretreated soil.

c. The carbon coating adsorbed the herbicide only around the rice seed. The remaining herbicide was still active and could enter rice seedlings through roots (e.g. amiben) or shoot (e.g. CP 53619, RP 17623 and 2,4-D IPE) shortly after the soil was flooded. Herbicide desorption from carbon and soil, which was not studied, might also

Unfortunately, many of these seeds were killed and those that survived showed some injury, although the degree of toxicity was significantly less than that of uncoated seeds. The causes of this mortality and/or injury can be attributed to one or more of the following factors:

a. The limited amount of activated carbon which could be pe11eted on rice seed even with triple coatings. Coating weight per seed varied from 9 to 17 mg. Its adsorption efficiency was even reduced further by at least 75 percent due to large reduction of surface area of carbon exposed to the herbicides, compared to that of carbon which remained as fine powder. Adsorption efficiency of carbon coatings appeared to be dependent on rate of herbicide diffusion and coating weight.

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occur to increase herbicide toxicity in soil (Bailey and White, 1970). For this reason, the survival of coated seed depends a great deal on the plant's ability to resist herbicide toxicity with increasing age. The faster recovery of coated seeds treated with CP 53619 compared to seeds treated with amiben was partly explained by this factor. For the same reason, 2-chloro-4-(ethylamino)-6-isopropylamino)-s-triazine (atrazine); 2-(ethylamino)-4(isopropylamino)-6-(methylthio)-s-triazine (ametryne); N,N-dimethyl-2,2-diphenylacetamide (diphenamid); 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron); 3-(hexahydro-4, 7-methanoindan-5-yl)-1,1-dimethylurea (norea) and other herbicides which are fatal to transplanted rice could not be protected by seed pelleting.

d. Flooding intensified herbicide toxicity. This factor was even more critical when the seedlings were still very young and water completely submerged them. Most of the coated seeds were killed by herbicides because they were sown on poorly drained soil.

e. The chance of survival was greater if the seedlings grew rapidly. In winter, cold temperatures inhibited growth rate which caused a prolonged contact between toxic herbicide and the seedlings. Many of the coated seeds which were killed in winter can be partly explained by this factor. It is not known whether growth hormones such as gibberillic acid will solve this problem, since it was found to increase growth rate even in low temperatures, when rice seeds were soaked in water containing 50 ppm gibberillic acid before sowing. This problem was not investigated due to lack of time. The questions are whether increased growth rate due to growth hormone will increase

herbicide toxicity, rather than decreasing toxicity, and whether increased growth rate has as adverse effect on grain yield or not.

Despite the above drawbacks, triple carbon-coated rice seeds yielded as much as the weeded control and sometime higher because the injured seedlings generally recovered with time, and IRS - being a high tillering variety - tillered profusely, thus compensating for many of the coated seeds killed at sowing. The rate of recovery was dependent on availability of the herbicide (which was determined by rate of application and the amount adsorbed by carbon coating), sensitivity of rice seed/seedlings to the herbicide, and its persistence in soil. 2,4-D IPE persisted in soil for only about 4 weeks. RP 17623 showed the longest persistence in soil, followed by CP 53619 and amiben. Severely injured seedlings generally delayed flowering by about 2 to 7 days even though they recovered completely.

The problem with granular herbicide was solved by applying them first on flooded soil then draining the soil about 7 days later to allow sowing of coated seeds on drained soil, and then reflooding it again when the seedlings reached 2 to 3-leaf stage. This preplanting application proved to be better than early postemergence application since in the latter application weed control was poor. However, it did not work well with herbicides which had high mobility in soil due to serious herbicide losses when the soil was drained at 7 days after sowing.

What is the chance of success of carbon-pelleted rice seed under a given herbicide? The answer depends very much on the properties of the herbicide. If the herbicide behaves like CP 53619, the chance

of success would be very good since (a) CP 53619 was highly adsorbed on activated carbon; (b) it was highly adsorbed on soil and also not easily leached; (c) its primary site of uptake was through the shoot which during the seedling stage, could be prevented by delaying flooding; and (d) the rice seedlings acquired resistance to the herbicide as soon as it reached ⁴ to ⁶ leaf stage (10 to ¹⁷ days after sowing).

The chance of success of carbon-coated seed treated with herbicides having properties like amiben, RP 17623 and $2,4$ -D IPE would be small under field conditions. The toxicity of 2,4-D IPE and amiben to coated seed was primarily due to the high sensitivity of rice seed to these herbicides, and secondly to relatively high mobility of the herbicides in soil. The concentrations at which 2,4-D IPE, amiben, CP 53619 and RP 17623 caused 50% reduction of root/shoot of IR8 were 0.14, 0.77,3.3 and 128.0 ppm, respectively. RP 17623 was toxic to coated seeds at the rates of 3.36 to 4.48 kg/ha partly because it did not diffuse readily to coated seed, with a consequence that most of it remained unadsorbed. In terms of total uptake in ⁴⁸ hr, 2,4-D showed the highest rate of diffusion to coated seed, followed by amiben, CP 53619 and RP 17623.

If the herbicide behaves like atrazine, the chance of success is practically nil since there was no way of preventing the entry of the highly toxic herbicide to growing rice seedlings. Carbon-coating was effective in protecting directseeded rice from an herbicide only when it was not lethal to transplanted rice.

Further advantages of seed pelleting were demonstrated by incorporating methiocard (4-methylthio-3,5-xylyl N-methylcarbamate) an experimental bird repellent - in the carbon pellet, a practice which effectively protected rice seed from birds as well as toxic herbicides. The toxicity of the insecticide to rice seed was also reduced by activated carbon by adsorbing it before being absorbed by seed.

Seed pelleting was not effective in protecting upland (nonflooded) rice from toxic amiben, diphenamid and atrazine. Further investigations are needed to solve this problem so that the technique can be used for other upland crops such as corn and sorghum. The toxicity of CP 53619 and RP 17623 could simply be reduced by planting rice seeds at least 3 em below soil surface but no deeper than 4.5 em. These two herbicides were highly selective to upland rice even at 4.48 kg/ha. Amiben and 2,4-D IPE were toxic to upland rice because they were easily leached and very toxic to emerging seedlings.

Sowing rice seed in upland soil is one of alternatives of obtaining herbicide selectivity in directseeded rice without seed pelleting. The soil can still be flooded, if need be, although greater amount of water is needed than if the soil is puddled. Other alternatives are: (a) the application of granular CP 53619 at 2 to 3 leaf stage of rice (De Datta and Bernasor, 1970), and (b) the application of the new herbicides benthiocarb (IRRI, 1971; Obien, et al., 1971) and RP 17623 at 1.1 kg/ha (Obien, et al., 1970; Smith and Fox, 1971).

CHAPTER XI. LITERATURE CITED

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