

est to measure the respiration rates of the fumigated and unfumigated termites. The results of this experiment showed a definite increase in the rate of oxygen uptake in the case of the fumigated insect. The respiratory quotient was increased from 0.5 to 1.0. The fluoride probably disrupts the basic energetics of the cell in some manner and increases the oxygen consumption by disturbing the interrelationships between inorganic phosphate, ADP, and ATP (6).

In the case of Vikane, then, the only path open to the fumigated termite for maintaining the necessary energy balance appears to be one involving the utilization of protein and amino acids. Since this source of internal food is probably not capable of increasing the metabolic rate sufficiently to keep up with or overcome the stress, the insect dies.

The general procedure described here has yielded a sizable amount of information which is readily susceptible to interpretation leading to an understanding of the mechanism of action of a toxicant in a biological system. The procedure

is flexible and of general utility since it requires only labeled acetate and phosphate and not necessarily labeled toxicant.

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Received for review April 30, 1962. Accepted August 9, 1962. Division of Agricultural and Food Chemistry, 140th Meeting, ACS, Chicago, September 1961.

## SOIL ADSORPTION OF HERBICIDES

### Adsorption of Several Pre-emergence Herbicides by Hawaiian Sugar Cane Soils

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The equilibrium adsorptions of fenuron, linuron, pentachlorophenol, simazine, and atrazine on Hawaiian sugar cane soils were compared to monuron and diuron. The adsorptive pattern for different soils was similar for the different herbicides; the major differences were in the quantitative adsorptivity level of a given chemical and were in the order pentachlorophenol  $\geq$  linuron  $>$  diuron  $>$  simazine  $>$  monuron  $>$  atrazine. Empirical conditions for Freundlich isothermal adsorption were followed at most concentrations. Adsorptive behavior of these soils was found to be a property of soil mineral fraction (minor for most soils), easily oxidized organic fraction, and carbon arising from cane leaf burning. The latter two were considered major factors.

IN A PREVIOUS COMMUNICATION (4), a study was made of the equilibrium adsorption and desorption characteristics of a number of Hawaiian sugar cane soils for the two pre-emergence herbicides: monuron, 3-(*p*-chlorophenyl)-1,1-dimethylurea, and diuron, 3-(3,4-dichlorophenyl)-1,1-dimethylurea. The data obtained established that Hawaiian topsoils were generally highly adsorptive and that the isothermal equilibrium adsorption obeyed the Freundlich equation.

The present study extends the previous work to the comparison of monuron and diuron with two other substituted urea herbicides: fenuron, 3-phenyl-1,1-dimethylurea, and linuron, 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea [the Du Pont Co. has proposed formally to

K-62 Committee of the American Standards Association that the term linuron be established as the approved common (generic) name]; with two substituted triazine herbicides now in common use in Hawaii—simazine, 2-chloro-4,6-*bis*-(ethylamino)-*s*-triazine, and atrazine, 2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine; and with pentachlorophenol (PCP). While PCP has not been considered a pre-emergence herbicide in the usual sense, its excellence as a contact weed seedicide has led to its use in irrigation water prior to sugar cane emergence. In this application, soil becomes important to the extent that it removes the PCP from available soil solution and that it is a major factor in protecting the crop root system from contact with the chemical.

#### Experimental

**Adsorption of Substituted Urea Herbicides by Soils.** An aqueous solution, 100 ml., containing from 5 to 10  $\mu$ g. per ml. of the respective herbicides, purified by repeated crystallization, and 2.5 grams of  $K_2SO_4$  per liter as a flocculent, was shaken with 50 grams of air dry soil for 15 minutes. The soil had been ground and screened to pass a 2-mm. mesh screen. The suspensions were filtered through Whatman No. 12 paper, and the clear filtrates were analyzed by hydrolysis to the substituted aniline followed by steam distillation, diazotization, and coupling with *N*-1-naphthylethylenediamine according to the method of Young and Gortner (3).

**Adsorption of Substituted Triazine Herbicides by Soils.** SIMAZINE. An

aqueous solution, 40 ml., containing 2.5  $\mu\text{g}$ . per ml. of simazine-C<sup>14</sup> and 2.5 grams per liter of K<sub>2</sub>SO<sub>4</sub> was shaken with 20 grams of air dry soil. The filtrates, from treatment similar to the substituted urea herbicides, as 5-ml. aliquots, were dried in aluminum planchets, and counted in an end-window Geiger counter.

**ATRAZINE.** An aqueous solution, 50 ml., containing 2.5 grams of K<sub>2</sub>SO<sub>4</sub> per liter and 20  $\mu\text{g}$ . of purified atrazine per ml. was shaken with 25 grams of air dry soil. The clear filtrates were read against a soil blank of the same soil, shaken with K<sub>2</sub>SO<sub>4</sub> solution, on a Beckman Model DU spectrophotometer at 263 m $\mu$ , slit 0.01 mm. Comparison was made with a standard curve. Sensitivity at 263 m $\mu$  was 2  $\mu\text{g}$ . per ml. against a soil blank, precision 2  $\mu\text{g}$ . per ml. on four samples.

Alternatively, a 15-ml. aliquot of the filtrate after adsorption was placed in a 25-ml. volumetric flask with 1 ml. of 1 to 1 sulfuric acid to water and was heated in a water bath at 80° to 90° C. for 2 hours. The solution was cooled, diluted to volume with K<sub>2</sub>SO<sub>4</sub> solution, and read against a soil blank of the same soil, similarly treated, at 240 m $\mu$  as hydroxy-atrazine. Hydrolytic replacement of the chlorine atom of the original atrazine was complete by this treatment.

Although the absorbance differences at 240 m $\mu$  are about sixfold greater per microgram of hydroxyatrazine than at 263 m $\mu$  for atrazine, the latter was reproducible and sufficiently precise for the work reported; considerably less manipulation was required at the latter wave length. K<sub>2</sub>SO<sub>4</sub> did not interfere at either wave length; however, an attempt to utilize the atrazine peak at 222 m $\mu$  was unsuccessful.

**Adsorption of Pentachlorophenol by Soils.** An aqueous solution, 100 ml., of purified PCP, containing 10  $\mu\text{g}$ . per ml. and 2.5 grams of K<sub>2</sub>SO<sub>4</sub> per liter was shaken with 50 grams of air dry soil and filtered as before. The clear filtrates were acidified with H<sub>3</sub>PO<sub>4</sub> and extracted with chloroform. The PCP was

extracted from the chloroform with 25 ml. of aqueous 0.1 N NaOH and read as sodium pentachlorophenate at 320 m $\mu$  against a prepared standard. Sensitivity was 1  $\mu\text{g}$ . per ml. on the sodium salt volume.

**Organic Matter and Carbon Determinations.** Fifty grams of air dry soil was placed in a dish in a muffle furnace and heated for periods of time up to 24 hours at 500° to 575° C. The monuron adsorption of the partially oxidized soil was determined as above. In some cases, carbon removal seemed to be complete after 24 hours. Heating at this temperature undoubtedly affected the structure (and adsorptivity) of the soil.

Removal of the organic matter with minimum soil alteration and without destruction of carbon was accomplished by wet oxidation of 50 grams of soil with successive 10- to 20-ml. portions of 30% hydrogen peroxide (7). Ten portions of oxidant were used; the mixture was heated gently on a steam bath until each portion had reacted and evaporated. Soils containing manganese will continue to decompose peroxide; frothing could not be used as evidence of incomplete organic oxidation. Soil adsorption for monuron was determined on the oxidized samples.

## Discussion

**Equilibrium Adsorption of Substituted Ureas.** Ten soils from sugar cane fields, representing a variety of soil groups and known to represent a range of monuron and diuron adsorptions were selected for most of the measurements reported herein. A supplemental tabulation of a few properties of these soils is contained in Table I. In Figure 1, the equilibrium adsorption capacity of each soil for each of the four substituted-urea herbicides is shown for a standard set of conditions. The trends, both for soils and herbicides, suggest a similar adsorptive mechanism with differences between the chemicals in polarity. Phenylurea (not shown) resembles fen-

uron. Phytotoxicity increases in the order fenuron < linuron  $\leq$  monuron < diuron, while water solubility is in the order diuron < linuron  $\leq$  monuron < fenuron. In spite of the recognized superior toxicity of diuron, its high adsorptivity and low aqueous solubility have limited its usefulness on certain soils in Hawaii. Although diuron is intrinsically more toxic to sugar cane than monuron, the same factors of adsorption and low solubility have limited the frequency of observed injury under actual use conditions. Experimental observations on linuron have shown parallels with diuron in many respects both as a pre-emergence for sugar cane and as a treatment for emerged weeds. Linuron has not proved to be consistently better in field trials than either monuron or diuron in Hawaiian soils. Its high adsorptivity has limited the appearance of sugar cane injury symptoms, while its relatively low saturation solubility (75  $\mu\text{g}$ . per ml.) in water may limit the degree of weed control in dry areas over that found with monuron.

Isothermal adsorptions with varying

**Table I. Some Properties of 10 Sugar Cane Topsoils**

Soil	Monuron Adsorption (%)	pH	P Fixation (%)
OS-RS, Mixed Kah-5, Gray	75	5.4	76
Hydromorphic Kah-47, Alluvial	76	6.7	54
Kah-4, Regosol	61	6.1	66
McB-14F, Low Humic Latosol—Kahana	32	8.0	27
McB-9F, Low Humic Latosol—Molokai	55	6.2	78
LP-38A, Humic Ferruginous Latosol	51	5.3	86
WS-105, Alluvial	46	5.3	90
GF-K24, Reddish-brown soil	15	6.6	84
Olo-140, Dark magnesium clay	48	4.4	82
	55	7.6	81

**Table II. Effect of Removal of Soil Organic Fractions on Monuron Adsorption by Soils**

Soil	Horizon (inches)	Original Soils		H <sub>2</sub> O <sub>2</sub> -Treated Soils			Ignited Soils				Weight loss (%), 500° to 575° C., 24 hours		
		pH	P fixation (%)	Monuron adsorption (%)	pH	P fixation (%)	Monuron <sup>a</sup> adsorption (%)	Weight loss (%)	Monuron adsorption (%)				
									250° to 275° C., 3 hours	500° to 575° C., 3 hours		14 hours	24 hours
HC&S-715	A 0-7	7.2	79	76	6.9	84	68	8.0	84	100	62	53 <sup>b</sup>	18.9
Low humic latosol	B 19-30	7.1	91	45	6.8	90	38	2.4	48	85	72	63 <sup>b</sup>	21.0
	C 43-51	6.9	77	17	6.7	85	17	10.0	48	82	83	72 <sup>b</sup>	18.9
Hilo-50	A 0-14	5.0	99.3	68	4.7	99.0	16	9.8	82	100	..	5	37.0
	B 14-28	5.7	99.6	17	5.5	99.2	4	20.0	24	100	..	3	42.9
Honokaa-5a	A 0-10	5.2	99.3	71	4.6	95.6	30	19.8	84	100	..	3	45.0
	B 10-18	5.3	99.3	29	5.2	97.4	7	28.0	57	100	..	5	48.7

<sup>a</sup> Based on 50 grams of original soil. <sup>b</sup> Incomplete ignition of carbon.

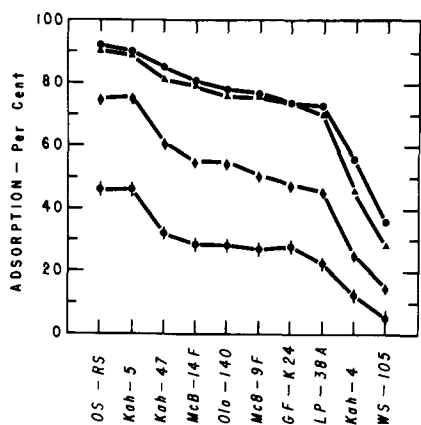


Figure 1. Equilibrium adsorption at single solution concentration of linuron (●), diuron (▲), monuron (◆), and fenuron (●) on 10 sugar cane soils

concentrations of linuron on several soils are shown in Figure 2. As with monuron and diuron, the empirical Freundlich equation is satisfied over the range of concentrations; the slope of the lines (0.9 to 0.95) and the  $K$ -values (at  $C = 1$ ) closely correspond with those of diuron. Figure 3 shows the equilibrium desorption values obtained by successive aqueous dilution after adsorption of the chemical by the soil. A pattern essentially similar to that of monuron and diuron was found for linuron in which soils of high adsorptivity released relatively little on dilution while linuron adsorbed on a soil of low adsorptivity was released with comparative ease. The smaller slopes (0.6 to 0.65) for the desorption plots compared with adsorption would suggest that under dynamic field conditions somewhat higher soil solution concentrations may exist than would be apparent from the adsorption curves. However, it must also be considered that the laboratory conditions exaggerate the normal soil to moisture relationship and that lower moisture levels shift the adsorption and desorption equilibria toward a greater degree of adsorption.

**Equilibrium Adsorption of Pentachlorophenol.** The single point adsorption values for the 10 selected soils, using an aqueous solution containing 10  $\mu\text{g.}$  of PCP per ml., are presented in Figure 4. Pentachlorophenol adsorption superficially resembled that of diuron, and the adsorption had no apparent relationship to soil pH. This is not too surprising in view of the fact that high basic strength is necessary to convert PCP to its salts. However, PCP was expected to show more deviation from the pattern of the urea herbicides. The  $\log \times \log$  plots of four soils in Figure 5 indicate wide variation in  $K$ -values at  $C = 1$  from an apparent 0.01 for the low adsorptive WS-105 to 21 for the highly adsorptive

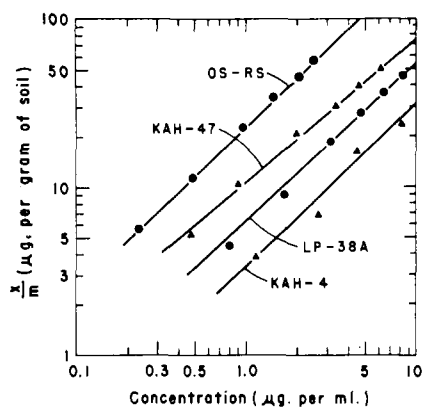


Figure 2. Equilibrium adsorption variation of linuron with concentration on four sugar cane soils

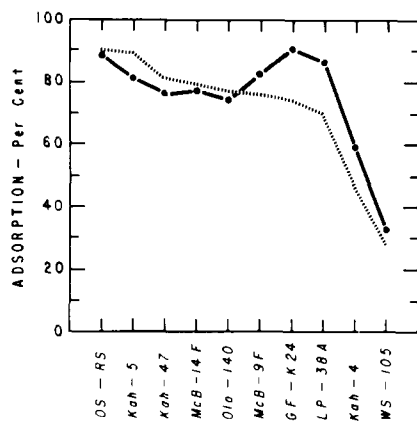


Figure 4. Equilibrium adsorption at a single solution concentration of pentachlorophenol (●) compared with diuron (dotted line) on 10 sugar cane soils

GF-K24. Although shown as a linear plot, the WS-105 points may not follow a straight line. With a herbicide as insoluble in water as PCP, it was difficult to get a sufficient range of concentrations. No work was done with sodium pentachlorophenate; it would be expected to act more like an exchangeable anion than the free phenol since insoluble salts are easily formed by reaction of sodium pentachlorophenate solution with many cations such as ammonium, calcium, and iron.

The application of PCP in irrigation water to control weed seed before germination has been successful only in soils of low adsorptivity. Where this is the case, relatively small amounts of PCP are needed, on the order of 10 to 20 pounds per acre, for excellent weed control. Seed has germinated only along the top line of the wetted perimeter; water apparently has been carried upward by capillary action for a short distance without carrying PCP with it. Similar field observations have been made whether the PCP was applied as

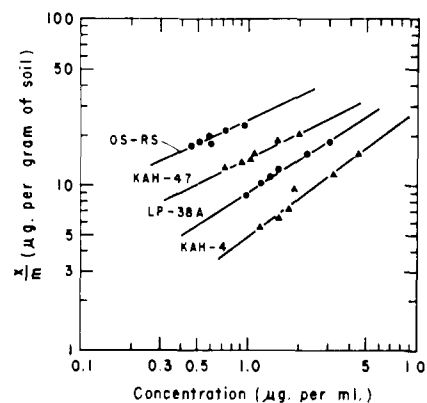


Figure 3. Equilibrium dilution (desorption) of linuron on four sugar cane soils

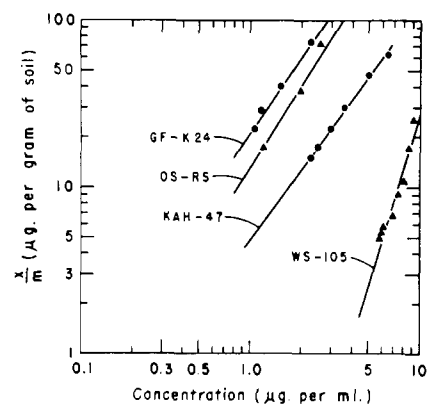


Figure 5. Equilibrium adsorption variation of pentachlorophenol with concentration on four sugar cane soils

an emulsified oil solution or as the sodium salt, although relatively few replicated comparisons have been made. In highly adsorptive soils, only partial to poor control has been obtained. The most interesting observation has been that excessive rates of application up to 500 pounds per acre gave little better weed control than 50 pounds. The steep slopes of the adsorption isotherms (1.5 to 3 of the  $\log \times \log$  plots) would suggest that large increases of PCP would be required for a significant increase of chemical in the soil solution.

Pentachlorophenol is severely phytotoxic when applied to sugar cane root systems. The leaf sheath wrappings tend to protect the meristematic tissue and stalk from accidental contact injury by above-ground sprays. Protection for the root systems must be supplied by the soil cover in preventing excessive leaching. Experimental rates of 1000 to 2000 pounds of PCP per acre as the emulsified oil solution have not injured sugar cane when applied to normal Hawaiian topsoils; more leaching and

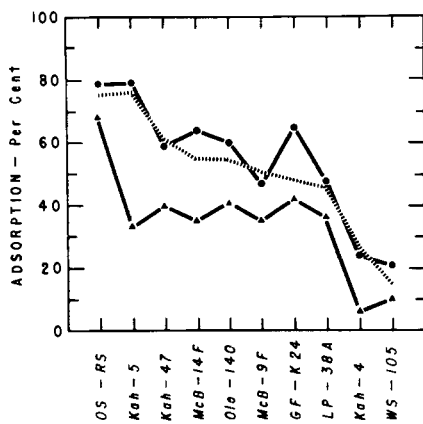


Figure 6. Equilibrium adsorption at a single solution concentration of simazine (●) and atrazine (▲) compared to monuron (dotted line) on 10 sugar cane soils

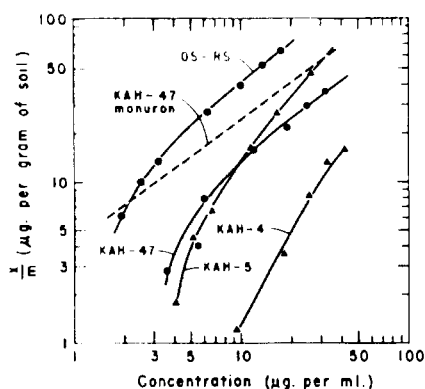


Figure 7. Equilibrium adsorption variation of atrazine with concentration on four sugar cane soils

cane injury has been evident with the sodium pentachlorophenate solutions.

**Equilibrium Adsorption of Simazine and Atrazine.** The two substituted triazines, simazine and atrazine, were made available for use in sugar cane in 1959 and 1961, respectively. Since sugar cane, like corn, has the ability to detoxify these chemicals at a reasonable rate for most application levels, a study of their adsorption phenomena has been used less to prevent crop injury and more as a guide to the most efficient and economical use for weed control.

Simazine proved difficult to work with because of its low water solubility (3.5  $\mu\text{g. per ml.}$  was the maximum used). A supply of simazine- $\text{C}^{14}$  was available; however, soil samples must be run in triplicate or more to obtain sufficient precision. The reasons for this are unknown; probably the low simazine concentration, small sample aliquot size, effect of heat in drying the samples with infrared lamps, and self-absorption from the potassium sulfate and soil extractants all contributed. In general, the adsorptive pattern of simazine from single

#### USDA / HC & S Co. SOIL PROFILE ADSORPTIONS OF MONURON & DIURON

DEPTH - INCHES	FD. 903 CATANO SANDY	FD. 809 WAIANAE GRAVELLY SILTY CLAY	FD. 715 PUUNENE SILTY CLAY	FD. 603 MOLOKAI SILTY CLAY LOAM	FD. 406 KEAHUA SILTY CLAY LOAM	FD. 311 KEAHUA SILTY CLAY	FD. 201 PAIA SILTY CLAY	FD. 103 MALIKO SILTY CLAY
	M D	M D	M D	M D	M D	M D	M D	M D
0	30 52	58 79	76 89	64 84	55 76	62 81	62 81	52 74
12	39 65	40 65			17 34	60 81		
24	8 20	17 33	45 71	11 13	9 14	13 22	13 18	8 11
36	7 13				7 7		12 17	
48	6 8	13 26	17 24	7 12		8 12	8 9	8 7
60								

M = MONURON  
D = DIURON

Figure 8. Profile adsorptions for monuron and diuron on eight sugar cane soils

point data followed that of monuron (Figure 6), with some notable exceptions: one soil, Kah-9, not included elsewhere in this study, adsorbed 21% of the monuron but 87% of the simazine- $\text{C}^{14}$ . Two other such widely divergent results were obtained in the course of studying some 50 to 60 soil samples. Aside from the difference in herbicide analysis, there was no apparent explanation for these variations.

While the plots of Figure 6 would indicate a reasonable degree of correspondence between the adsorptive behavior of monuron and atrazine, a greater variability has been found than was true between monuron and diuron. Figure 7 presents the atrazine isothermal log  $\times$  log plots for several soils where the solution concentration was varied from 3.5 to 25  $\mu\text{g. per ml.}$  of solution. The slopes of the lines were variable indicating considerable deviation from the empirical Freundlich equation. The deviation was most apparent at low concentrations of atrazine. Simazine would be expected to show similar behavior if a range of concentrations could be achieved.

Soil blanks were necessary for each soil as there was considerable extraction of soluble substances having some degree of absorption at 263  $\mu\text{m}$  as well as at 240  $\mu\text{m}$  for the hydrolyzed solutions. The amount of extracted substances which showed ultraviolet absorption varied for each soil blank. Interference became severe below 230  $\mu\text{m}$  prohibiting the use of the major atrazine peak at 222  $\mu\text{m}$ .

An attempt was made to use  $\text{BaCl}_2$  as a flocculent instead of  $\text{K}_2\text{SO}_4$  since it had been used (2) to measure the flocculent volume of soils as a function of particle size. The  $\text{BaCl}_2$  was a superior flocculent and, as  $\text{BaCl}_2$ , gave no ultraviolet inter-

ference. However, some soil extracts showed evidence of reactions which produced interference; further, a thin adherent film tended to form on the absorption cells with use.

**Adsorptive Factors in Hawaiian Sugar Cane Soils.** Insufficient data are available to give a very detailed quantitative explanation for the observed soil phenomena. In preliminary tests, no correspondence was found with base exchange capacity, pH, particle size, phosphate fixation, or organic matter (by the chromic acid method). Separation of the surface soils by soil family provided at best a rough grouping.

It is suggested that at least three distinct types of adsorptive sites are available in these soils, each possessing a unique degree of availability and bonding energy.

The soil mineral fraction undoubtedly contributes a part of the adsorptive capacity. Soil profile studies, made in cooperation with the Hawaiian offices of the U.S.D.A. Soil Conservation Service and the Hawaiian Commercial and Sugar Co., (Figure 8) showed that the soil adsorption for monuron and diuron dropped rapidly below the depths where soil mixture (plowing) and where the major organic fraction occurred. This means that for most soils the condition of the topsoils was mainly responsible for high adsorptive values. The soil mineral fraction, from this and other profile studies and from ignited samples, seemed of relatively little importance.

The second factor, of considerably more importance, appeared as the supply of organic matter in the topsoils. This is defined for present purposes as the decomposing supply of cane roots, leaves, stumps, and mill effluent mud and water. Sugar cane grows in Hawaii for 2 years;

at the end of this time, 10 to 15 tons of roots per acre are left to decompose whether the new crop is grown from stubble (ratooned) or completely replanted. Further, the sugar cane leaves, discarded at the rate of one leaf in approximately 14 days as a new leaf is formed, provide a mat, part of which (depending on climate) decomposes or leaches into the soil. Wet oxidation of this fraction with hydrogen peroxide has shown that the soil adsorption capacity for monuron decreased nearly to the subsoil values, provided that no free carbon was present in the soil (Table II, Hilo, A).

True carbon provides a major source of herbicide adsorptive capacity in Hawaiian sugar cane soils. Just prior to harvest, sugar cane fields are burned to facilitate mechanical harvesting by removal of as much of the leaf trash and tops as possible. In dry areas or in dry seasons, the burns will be relatively complete but will supply a considerable quantity of particulate matter, more or less completely carbonized. The total quantity may not be large in comparison with soil volume, but the adsorptive capacity is high and the pre-emergence

herbicides are applied for the new crop generally within 2 to 3 weeks after harvesting. Areas with greater rainfall have less carbon due to poor burning of wet trash and in limited areas there is no attempt to burn unless conditions are very favorable.

Unfortunately, conventional wet methods for determining organic matter in soil do not oxidize carbon and combustion methods affect soil water, bicarbonates, and other minerals, and do not distinguish between organic forms. Further, it is doubtful that organic residues in soils of different climates decompose at the same rate or even to the same products.

Table II summarizes a series of oxidations with  $H_2O_2$  and ignition on several horizons of three soils. HC&S-715 comes from a dry climate with good burns; its topsoil adsorption remained high even after peroxide treatment. Hilo-50 soil is from a wet climate with poor burns; its topsoil adsorption was reduced markedly with peroxide and completely on ignition. Honokaa-5a is from an intermediate climate with fair burning conditions for part of the year; its properties were apparently interme-

diated with complete removal of adsorption on ignition.

### Acknowledgment

Acknowledgment is made to the Geigy Chemical Corp. for the simazine- $C^{14}$ , Reichhold Chemical Co. for purified PCP, George Uyehara for analysis of PCP, and Constance Hartt for radioactive counting.

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Received for review March 1, 1962. Accepted July 9, 1962. Division of Agricultural and Food Chemistry, 141st Meeting, ACS, Washington, D. C., March, 1962. Presented with the approval of the Director as Paper No. 109 of the Journal Series of the Experiment Station, Hawaiian Sugar Planters' Association, Honolulu 14, Hawaii.

## HERBICIDE RESIDUES

# Determination of Micro Amounts of Isopropyl *N*-(3-Chlorophenyl)carbamate (CIPC) in Milk and Urine Excreted from Dairy Cows

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Sensitive analytical methods for determining micro amounts of the herbicide CIPC in milk and urine from dairy cows were needed in connection with feeding tests. The developed analytical methods entail extraction, hydrolysis, and spectrophotometric techniques as a basis of measuring CIPC residues in the samples. Results from fortified and aged samples show recovery of CIPC ranging from 75 to 80% at the 0.1 p.p.m. and 0.025 p.p.m. concentration levels, respectively. The methods are applicable to analysis of milk produced by dairy cows who have eaten forage crops treated with CIPC for weed control.

DURING the past several years, isopropyl *N*-(3-chlorophenyl)-carbamate (CIPC) has been used experimentally as a pre-emergence and postemergence herbicide to control the growth of narrow-leaved plants, such as crabgrass, wild oats, and witch grass (3). This herbicide was first used in the production of food crops such as lettuce, sugar beets, onions, tomatoes, spinach, and carrots. Success in these applications encouraged its experimental use in the production of forage crops, such as alfalfa, with good results.

It is very important to determine the amount of CIPC or its metabolite, 3-chloroaniline, in milk produced by dairy cows consuming forage crops treated with this chemical. Simultaneously with this determination in the milk, it is of interest to determine the amount of CIPC or its metabolite, which is excreted in the urine.

During May and June, 1961, a cooperative program was instituted between the Pittsburgh Plate Glass Co., Chemical Division, and the Ohio Agricultural Experiment Station,

Wooster, Ohio, to conduct feeding studies (5) wherein known amounts of CIPC were introduced in the daily rations of grain given to dairy cows. These feeding studies were conducted as a part of a program wherein the selection of the test animals, administration of the fortified diet, and the sampling and analytical procedures were carried out according to accepted practices. The results of this feeding study will be reported elsewhere.

Basic spectrophotometric procedures for determining micro amounts of