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9. ABSTRACT

Organic matter is the principal absorbant of such herbicides as Atrazine, Ametryne, Diuron, Dalapon, and 2,4-D, which are used in sugarcane fields in Hawaii. Charcoal from cane burning is thought to contribute to herbicide adsorption, thus retarding its movement. Once a herbicide moves below the plow layer, which contains most of the organic matter and charcoal, its mobility may increase several fold. Herbicides and fertilizers applied to the soil move very small distances by molecular diffusion. Movements of more than an inch occur only in moving soil water. However, the large quantities of rain or irrigation water received by sugarcane soils can transport applied chemicals downward 'f soil colloids do not retard their movement. The nature of water and solute movement in the subsurface rock is not precisely known. The main mass of lavas underlying Oahu have a fairly high porosity and permeability, with total porosity estimated at as high as 25%. In any event, it is apparent that applied nitrates and sulfates move through the soil profile into ground waters, but much less evident that herbicides do to an extent sufficient to cause concern about the threat to ground water quality from this source. Even with current irrigation practices, herbicide transport to groundwaters can be maintained at negligible levels by the use of chemicals which are adsorbed on soils and are only moderately persistent. Current pesticide registration procedures are sufficiently stringent to preclude use of materials having both high mobility and high persistence. Nevertheless, selected well waters should be periodically monitored.

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HERBICIDE AND FERTILIZER MOVEMENT IN HAWAIIAN SUGARCANE SOILS IN RELATION TO SUBSURFACE WATER QUALITY

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The movement of agricultural chemicals in soils has long been a matter of interest to cane producers in Hawaii. Both native and applied nutrients may be lost by leaching below the root zone under conditions of high rainfall or abundant irrigation. The desirability of conserving nitrogen and potassium, in particular, has prompted numerous evaluations of nutrient uptake and leaching in both field and lysimeter studies by the Hawaiian Sugar Planters' Experiment Station. The adsorption and leaching of herbicides has received considerable attention also, principally from the standpoint of residues and effective weed control. Concern for the quality of subsurface waters has prompted additional interest in the mobility of chemicals in soils. In the Pearl Harbor area of Oahu alone the daily volume of water pumped from wells is about 160 million gallons, most of which is used for irrigation of sugarcane (Visher and Mink, 1964). The increased demand placed on the water resources of Oahu by an increasing population and attendant urban development requires continued study of the amount and quality of water available for a variety of uses.

In this paper we will describe the numerous factors known to affect transport of chemicals in moving soil water and relate these factors to results of experiments performed in Hawaii and elsewhere. It is hoped that such an analysis will contribute to an informed understanding of the relationship between subsurface water quality and the use of agricultural chemicals in cane production.

The Chemicals

Herbicides

The total quantities of herbicides used in cane in 1968 are listed in Table 1. Information on leaching and breakdown of dalapon, 2,4-D, and TCA is somewhat limited for Hawaiian soils, but results from the literature allow prediction with reasonable confidence. The preemergence herbicides atrazine, ametryne, and diuron are highly adsorbed in most soils in Hawaii, especially those high in organic matter (Hilton and Yuen, 1963; Suehisa, 1967). Dalapon, 2,4-D, TCA and pentachlorophenol are all much more mobile in high pH soils than in the more acidic soils common to Hawaii. The mobility of these compounds under neutral to alkaline conditions is due to their ionic character. With increasing pH they become increasingly polar as organic anions, resulting in increased solubility in water and decreased adsorption on soils having a high net negative charge. Atrazine and ametryne, although much less sensitive to pH, become positively charged at low soil pH values, and thus are readily attracted to negatively charged soil organic matter and clay minerals (Yamane and Green, 1971) resulting in decreased mobility.

The disappearance of herbicides from surface soils depends on microbial and chemical degradation as well as leaching. It is significant that the more mobile herbicides above are much more rapidly degraded in soils than the less mobile herbicides. The low mobility and high persistence of atrazine, ametryne, and diuron are important to the favorable performance of these herbicides for preemergence weed control. Fortunately, none of the materials used in sugarcane have the undesirable combination of high mobility and high persistence which might be detrimental to subsurface water quality.

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Table 1. Herbicides Used in Sugarcane, Hawaii, 1968

Herbicide	Total[1/] Used in Sugarcane, 1968, (lbs.active)	Approx. Rate,[2/] (lbs.active/acre/crop)	Solubility[3/] in Water	Leaching[3/,4/]	Breakdown[3/,4/]	Toxicity, Acute Oral LD_{50} for Rats (mg/kg)
Atrazine	293,000	6 to 8 (in 2 appl., usually with diuron or ametryne)	40 ppm	slow	Acid soils-rapid; Neut.soils-slower	3080
Ametryne	330,000	6 (principally in irrigated areas)	185 ppm	slow	Similar to atrazine	1110
Diuron	512,000	6 (principally in wet areas)	42 ppm	slow	Moderately slow	3400
Dalapon	546,000	1.5 to 3 (spot spray) only 1/2 or less used in-field	50g/100g	Acid soils-moderate; Neut.soils-rapid	Rapid (few weeks)	7570
2,4-D	197,000	3 to 4 (special areas only)	650 ppm	"	Rapid (few weeks)	300 to 1000
TCA, sodium[5/]	339,000	5 lbs/application with 4 to 6 applications;(limited use now)	83g/100g	"	Slower than Dalapon	5000
Pentachlorophenol[6/]	347,000	"	30 ppm	Acid soils-slow; Neut.soils-moderate	---	80

1/ Kimura and Hurov, 1969.
2/ H.W. Hilton, personal communication.
3/ Weed Society of America, 1967 plus other references given in the text.
4/ Generalized to include most Island soils developed from volcanic materials, but not including sands.
5/ Not registered for use after 1970.
6/ Not registered for use after 1969.

Fertilizers

The use of N, P, and K fertilizers in cane production has been discussed in detail in numerous reports; only results pertinent to our present discussion will be cited. Cane generally requires per acre fertilizer applications in the range of 250-400 pounds N, 0-350 pounds P_2O_5 and 0-500 pounds K_2O, the quantities depending on a number of soil, climatic, and management factors. Quantities removed by a 100-ton crop are reported to be about 150-250 pounds N, 25-30 pounds P_2O_5 and 300-500 pounds K_2O (Humbert, 1968). Both N- and P-removal by the crop are considerably less than the quantities usually applied, whereas K applied and K removal appear nearly equivalent.

The mobility of fertilizer elements in Hawaiian soils varies with the elements and with the forms applied for N and K. Phosphorus movement is negligible in nearly all soils; potassium movement varies with soil type and the nature of the associated anion (Ayres, 1955); nitrogen moves relatively fast when it is in the nitrate form. Sulfur in the sulfate form, commonly found in N and P fertilizers, is more mobile than phosphate but less mobile than chloride often associated with K. Chloride and nitrate mobilities are very similar. We will not attempt a detailed description of the chemistry of these elements in soils, but will examine some of the properties of Hawaiian soils that result in the range of mobilities mentioned above.

Effect of Soil Properties on Mobility of Agricultural Chemicals

Soil Mineralogy and Chemistry

Although Hawaiian soils are all derived from materials of volcanic origin, they differ widely in mineralogy and chemistry. The nature of parent material (basaltic or andesitic Aa or Pahoehoe lava, cinders, ash, etc.), topography, climate, and vegetation all contribute to the extreme variation of soils planted to sugarcane in the Islands. Soils formed in low-lying, poorly drained areas are rich in montmorillonite and thus have a high cation exchange capacity--a property that accounts for the retention of potassium, calcium, and other cations by these soils. The red Low Humic and Humic Latosols in well-drained areas receiving 30-80 inches rainfall contain kaolin clays and iron oxides, and have relatively low cation exchange capacities. The mineral fractions of soils developed under high rainfall conditions, such as the Hydrol Humic Latosols of the Hamakua coast, are predominantly hydrated aluminum and iron oxides. They have very low base saturations (1-5%), i.e. their exchange complexes have high proportions of hydrogen and aluminum ions and low proportions of bases such as calcium or magnesium. Since K and NH_4 ions do not replace H and Al ions very effectively, these nutrient elements move rapidly through Hydrol Humic Latosols (Ayres, 1955). These latter soils are unique in many ways, but the lack of cation retention and a relatively high capacity for anion retention is important to chemical mobility. Whereas nitrate and chloride move almost with the moving water front in most soils, these anions are retained by Hydrol Humic Latosols (Ayres and Hagihara, 1960; Singh and Kanehiro, 1969). The mechanism of anion retention is more complicated than cation exchange but is closely linked to clay mineralogy and soil pH (anion adsorption increases with decreasing pH). Sulfate adsorption and phosphate adsorption are especially high in these soils (Hasan et al., 1970; Fox et al., 1968) so that movement of these anions is negligible. Phosphorus and sulfur are retained principally by electrostatic attractions or coordination with iron oxides and amorphous aluminum oxides in low pH soils (Mekaru and Uehara, 1971). The above discussion indicates that plant nutrient movement in soils is dependent primarily on soil mineralogy, base saturation, and pH, i.e. those properties which affect cation and anion retention.

Herbicide interaction with soils is more complicated, in that some herbicides vary in degree of charge or polarity with soil pH and some remain uncharged at all levels of pH. Organic matter is the principal adsorbent of all herbicides listed in Table I at normal field pH values; thus herbicide mobility is generally lowest on high organic matter soils. Charcoal from cane burning is thought to contribute substantially to herbicide adsorption

(Hilton and Yuen, 1966) and thus retards movement. Once a herbicide moves below the plow layer which contains most of the organic matter and charcoal, mobility may increase several fold. Only the Hydrol Humic Latosols have sufficient organic matter at lower depths to retard movement. The acidity and anion exchange properties of these soils will also contribute to slowing the movement of anionic herbicides such as 2,4-D.

Soil Structure and Water Movement

Herbicides and fertilizers applied to the soil move very small distances by molecular diffusion, while movement over distances of an inch or more must occur in moving soil water. The large quantities of water received by sugarcane soils as either rainfall or irrigation can transport applied chemicals downward if retention on soil colloids does not retard their movement. Although the lowland Gray Hydromorphic and Dark Magnesium Clay soils often have low sustained infiltration rates, most well-drained upland soils in Hawaii have high infiltration rates and are reasonably permeable throughout the profile. Thus a sustained infiltration rate of 2 to 4 inches per hour is not unusual; large volumes of water are required in furrow irrigation to accomplish movement of water to the ends of furrows. Six acre-inches of water per application is common in some areas, and near the head of the furrow total intake per irrigation exceeds the average field application rate considerably. The high permeability of these soils is due largely to the high degree of aggregation which provides sequences of macro-pores through which water can move rapidly when supplied in abundance. Small micro-pores within aggregates may be nearly filled with water even when the soil is dry enough to need irrigation. Water in these pores is thought to be unavailable to plants and does not contribute much to the vertical movement of water. This is important since a soil such as Wahiawa silty clay may contain 30% water which is essentially immobile (Sharma and Uehara, 1968; Cagauan, 1969). When one calculates the depth to which 6 inches of irrigation water might penetrate one needs to know how much air-filled pore volume can be filled with water and held against gravitational flow. Soil having a total pore space of 50% and an initial water content of 10% at irrigation might wet to a depth of 6/0.40 = 15 inches if all the pores filled with water. If 10% of the newly filled large pores were drained after one day, the water would have moved about 6/0.30 = 20 inches. The soil having 30% water in aggregate-pores at irrigation would conduct six inches of irrigation water to a much greater depth. Assuming 50% total pore space and 10% drained pores one day after irrigation, the wetting front would have moved 6/0.10 = 60 inches, a seemingly fantastic depth for one irrigation. Although sugarcane roots can penetrate to depts in excess of 5 feet in some soils, root growth is often restricted to the upper 2 to 3 feet (Trouse and Humbert, 1961). Water and chemicals which move below the principal rooting depth are likely to continue moving downward with subsequent irrigation or rainfall. It is under such conditions that mobile nutrients and herbicides may move into subsurface water sources and be transported in basal water to a well.

The nature of water and solute movement in the subsurface rock is not precisely known. The main mass of lavas underlying Oahu have a fairly high porosity and permeability. The total porosity has been estimated as high as 25 percent. Determinations of permeability in various holes and tunnels through the lavas have yielded permeabilities of 500 to 2000 gal/day per foot of drawdown per square foot of exposed area (Wentworth, 1951). Chemical weathering by oxidation, hydration, and carbonation of the various minerals of the basalt may result in a 15 to 25 percent expansion which reduces permeability of such weathered basaltic residuum. However, at depths below 75 feet the lava flows are in an unweathered condition and maintain their original porosity and permeability. Although the total porosity of the lavas is high, drawdown measurements on Oahu have indicated a "coefficient of storage", or porosity contributing to rapid flow, of about 5% (Visher and Mink, 1964). Thus a 3-inch surface depth of water draining out of the soil into the underlying rock might move 60 inches in the aquifer (3/0.05 = 60), the rate of movement depending on permeability and hydraulic gradient.

Fertilizer Movement

Among the chemical elements in fertilizers, nitrogen is of particular interest due to its high mobility as nitrate and the inherent toxicity of nitrate to humans (Bailey, 1968; U.S. Public Health Service, 1962).

Several studies by Takahashi (1964,1967,1968,1969,1970) with labeled nitrogen (N^{15}) in both lysimeters and field plots have indicated relatively low recovery of nitrogen in the cane plant (16 to 47% in several experiments at different locations), with about one-third to one-half of that recovered in the plant being in dead leaves. Leaching has not appeared to cause major losses, especially when the crop is well established and removes nitrate from soil solution throughout the rooting zone (Takahashi, 1964,1967,1968; Ayres and Hagihara, 1960). Ekern (1970) found that established cane growing in 5-foot deep lysimeters maintained a nitrate level of 1 ppm in the percolate even when the irrigation water contained 5 ppm nitrate. Subsequent removal of the crop resulted in an increased nitrate concentration in the percolate (10 to 15 ppm). Much of the applied nitrogen is apparently incorporated into the bio-mass and subsequently transformed into organic fractions which resist breakdown and thus limit plant uptake, breakdown, and movement. Lysimeter data on California soils reported by Dutt, et al. (1970) showed 20 to 26% of the applied nitrogen (labeled with N^{15}) in the soil after cropping one year with barley followed by sorghum; most of the residual nitrogen was near the surface and little was available to the second crop. Leachates contained less than 0.5% of the nitrogen applied, although a fairly large quantity of native nitrogen was leached. This may be an important fact, in that even though the fertilizer nitrogen fails to pass through the soil in large quantities, it may replace native nitrogen in the dynamic biological transformation of soil organic fractions. The free interchange of N^{15} with native soil N probably results in an isotopic dilution in surface layers of the soil that precludes much movement of labeled fertilizer, especially while a crop is growing. After the crop is removed, mineralization and nitrification may readily increase nitrates in the percolate.

At the present time it is not clear what happens to all of the fertilizer nitrogen applied to sugarcane soils, but the rapid movement of nitrate in soil water on most soils (Hydrol Humic Latosols excluded perhaps) indicates that leaching is one probable pathway of loss, especially during early stages of crop growth and under abundant furrow irrigation. The factors which influence nitrogen balance in the soil are numerous and interact in ways that preclude simple conclusions in a given case. This situation is not unique to Hawaii, as indicated by a discussion of nutrient mobility in various areas of the U.S. by Thomas (1970), but the variety of soils and water regimes in Hawaii make generalizations meaningless.

Chemical analyses of waters in numerous wells on Oahu and Maui during 1968-1969 have revealed apparent increases in nitrate and sulfate which are attributed to fertilizer applications to cane (Tenorio, et al., 1969). Oahu wells had nitrate levels generally below 5 ppm NO_3, while most Maui well waters contained 20 ppm and less. Visher and Mink (1964) give nitrate levels of 0.5 ppm in rain and uncontaminated stream water and 1.1 ppm in uncontaminated basal water. These investigators showed that wells in irrigated areas had nitrate levels six to eight times higher than wells outside irrigated areas.

The Maui data are particularly interesting in that the levels measured in given wells varied widely between four sample dates in a one-year period. For example, the Waikapu well (125 feet) had nitrate concentrations of 1.6, 22, 6.6, and 17 in four successive samples taken at intervals of two to six months; other wells showed similar variations. Aquifers in the Maui isthmus are presumably fed by water originating in West Maui and also by percolating irrigation water. It is interesting to speculate whether cycles in nitrogen application and irrigation could account for the striking nitrate variations observed in well waters. Tenorio (1970) observed for both Kahuku and Maui wells a distinct relationship between observed high values of nitrate and sulfate and increased pumping rates during dry periods. There were considerable time lags between the occurrence of peak solute concentrations and the times of irrigation at Kahuku, probably more lag than would

be required for infiltration to the water table. In the Maui wells there was a much more rapid response, though not instantaneous. Four principal factors that may directly influence the time it takes irrigation return water to reach the ground water table are: 1) the amount of natural recharge and irrigation water entering the basal water body, 2) the relative permeability of the aquifer, 3) the depth to the water table, and 4) the extent and variation in pumping practices at irrigation wells. A long transit time in the subsurface rock may be conducive to denitrification (Stewart, 1970). Denitrification could account for the lower relative increase in nitrate compared with the increase in sulfate observed by Tenorio et al. (1969).

In any event, it is apparent that applied nitrates and sulfates do move through the soil profile into ground waters. The Low Humic Latosols and Humic Latosols overlying pumped aquifers are reasonably efficient in retaining potassium but not nitrate and sulfate. Although nitrate levels for Hawaii well waters analyzed by Tenorio et al. (1969) are below the 45 ppm NO_3 (10 ppm N) considered maximum for potable waters by the U.S. Public Health Service (1962), the entrance of nutrients from irrigated fields into basal water supplies is reason for rational concern.

Herbicide Movement

All agricultural chemicals applied in irrigated areas need to be evaluated from the standpoint of subsurface water quality in addition to their efficiency with respect to crop production. There are no published results for Hawaii which describe field movement of the herbicides listed in Table 1, and no analyses for these materials have been performed on well waters. Some speculation on herbicide movement is warranted in that much is known about behavior of herbicides in soils. The rapid degradation of those compounds which are most mobile reduces the likelihood of these materials passing through the soil profile. Even the more persistent preemergence herbicides used in cane apparently degrade more rapidly in Hawaii than is common in colder, drier, more calcareous soils of temperate regions. Atrazine for example is a hazard to rotational cropping in most soils on the U.S. Mainland due to its long persistence, even though applied at low rates compared to those used in Hawaii. But studies with acidic Hawaiian soils show a rapid chemical hydrolysis of atrazine followed by slow total breakdown to CO_2 (Obien and Green, 1969; Goswami and Green, 1971). Ametryne and diuron degrade more slowly, but generally disappear in a period of several months.

Adsorption of herbicides retards movement also. However, adsorption on soils is largely reversible, so that herbicide adsorbed initially upon application will desorb into solution as the concentration in solution is decreased by plant uptake or moving soil water. Studies with diuron (Hilton and Yuen, 1966) and atrazine (Green, et al., 1968) have shown that both materials can be moved out of the soil by percolating water; high adsorption only delays the movement and spreads the material over greater distances so that it does not move in a concentrated band. If a herbicide is not entirely degraded in the slow migration downward, its mobility increases at lower depths due to greatly decreased adsorption in the subsoil. Thus it is possible for very small quantities to move into ground waters.

All things considered, namely the low quantities applied, relatively rapid degradation, plant uptake, and the delayed movement and dispersion caused by adsorption, it is unlikely that the herbicides presently used on cane will constitute a serious water quality problem. The importance of Hawaii's basal water supplies to the life and economy of Hawaii, however, does warrant the monitoring of wells and springs for trace organics, along with other solutes normally measured, to avoid any buildup of contaminants.

Management Implications

The likelihood of nitrate and sulfate movement under some conditions and the remote

possibility of some herbicides entering groundwaters suggest there may be a need for management alternatives which will contribute positively to the maintenance of high quality ground waters.

If percolation of water below the rooting zone can be reduced in irrigated areas, groundwater contamination by agricultural chemicals will be reduced. Considerable attention has been given in recent years to sprinkler irrigation of cane as an alternative to the less efficient practice of furrow irrigation. Sprinkler irrigation in itself does not reduce the movement of chemicals, since water applied by sprinklers at low intake rates may actually result in more extensive movement of solutes through the soil profile than the same quantity of water applied rapidly by furrow irrigation (Miller et al., 1965). However, sprinkler irrigation may allow use of only half as much water as is commonly applied by furrow irrigation in some areas (Campbell, 1963). The key is to reduce the total quantity of water applied in excess of evapotranspiration. Economic considerations will largely determine the further expansion of sprinkler irrigation, but improved water quality may be an additional "plus factor" for sprinklers.

Even with current irrigation practices, herbicide transport to groundwaters can be maintained at negligible levels by the use of chemicals which are adsorbed on soils and are only moderately persistent. Current pesticide registration procedures are sufficiently stringent to preclude use of materials having both high mobility and high persistence. Periodic monitoring of selected well waters would provide a safeguard against accumulation of persistent organic compounds.

An interest in increasing fertilizer N efficiency in cane production has motivated considerable research in the past, and additional studies are currently in progress at HSPA. Improvement in N efficiency is difficult in that optimum times and rates of application differ for each unique combination of soil and climate, and even from year to year. The use of slow-release N fertilizers may allow more control on the availability of N to the crop, and may reduce leaching. A careful accounting of all nitrogen available to the crop in relation to the crop's N requirement at a given time will help to avoid over-fertilization. Just as mineralizable N in the soil contributes significantly to N nutrition of sugarcane (Stanford et al., 1965), the quantity of N in irrigation water from some wells may also be high enough to be considered in calculations of fertilizer needs.

The sugar industry has played a key role in the development of groundwater in Hawaii and can, with positive management, assist in maintaining the high quality of this unique and valuable resource.

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