STUDIES ON ADSORPTION AND PERSISTENCE OF ATRAZINE IN SELECTED SOILS OF KARNATAKA

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STUDIES ON ADSORPTION AND PERSISTENCE OF ATRAZINE IN SELECTED SOILS OF KARNATAKA

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Dedicated to

My Beloved Parents

B. R. Anantha Rao

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CERTIFICATE

This is to certify that the thesis entitled "STUDIES ON ADSORPTION AND PERSISTENCE OF ATRAZINE IN SELECTED SOILS OF KARNATAKA" submitted by Mr.B.A. VADIRAJ for the degree of MASTER OF SCIENCE (AGRICULTURE) in SOIL SCIENCE of the University of Agricultural Sciences, Bangalore, is a record of research work done by him during the period of his study in this University under my guidence and supervision, and the thesis has not previously formed the basis of the award of any degree, diploma, associateship, fellowship or other similar titles.

BANGALORE,
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INTRODUCTION

I. INTRODUCTION

The use of pesticides in agriculture has become very essential in the modern concept of scientific farming. Starting from 1940's there has been substantive growths of pesticides application in agriculture. However, phenomenal increase in pesticide use commenced from the mid 1960's with the introduction of high yielding varieties. The development of high yielding varieties together with the application of agricultural chemicals have substantially increased the production of food grains in India which is almost commensurate with the increasing rate of population.

In India a large varieties of crops are grown under varying agro climatic conditions. More intensive the cropping practice we adopt, more is the need for applying pesticides to combat the enemies of crop plants. The damage caused to crops due to innumerable field pest has been estimated at about 30 per cent of the total production per year. Over the past few decades more than 1000 pesticides have been developed in the world, of which about 100 are in wide use. Presently, about a million tonnes of active ingredients (a.i.) of pesticides are manufactured in the world. However, theier application in different parts of the world varies widely depending upon the technical advancement of the country in respect of crop production.

The use of plant protection chemicals need to stay in India in view of the pressing demand for more production to keep pace with ever increasing population and to attain self sufficiency in food production. Among the different chemicals used, the s-triazines are the herbicides which are widely used as both for pre-emergence and post emergence application for industrial and agricultural purposes.

The fate of s-triazines in the soil is one of the most important aspect concerning their wide spread use. Their behaviour in soils determines the amount of weed control obtained, selectivity, persistence, effect on soil microorganisms, soil and water contamination and crop rotation. The applied herbicides must survive in soil environment long enough to kill the undesired weeds. However, if their persistence is too long, they need to be tested in different cropping systems to avoid more susceptible crops in the systems.

The more man's technology develops, the more important it becomes to study its influence on environment like soil, water, air, flora and fauna. This is mainly a matter of public concern. All the organic compounds added to the soil must ultimately decompose or to be altered to become the part of the soil complex. The nature and speed of alteration or loss are determined by the intricate interaction of the chemical and physical properties of the herbicide and the chemical, physical, edaphic and biological properties of the soil. The triazines are reported to be highly adsorbed on soil particles, there by showing high persistence. Thus there is a definite need to study their behaviour in all types of soil to avoid or minimise environmental pollution and also to choose proper crops in rotation.

Ion uptake capacity of the roots is one of the parameters affecting the efficiency with which a plant recovers nutrients from the soil. Therefore, any agricultural practice interfering with the uptake process can affect the absorption capacity of roots. Since the use of herbicides for control of weeds is common in modern agriculture, question arises wheather this practice can affect the uptake of nutrient by the plants. Even though, work on the transformation of herbicides in soil and the mechanisms with which they kill plants, are going on, little information is available regarding their direct effect on nutrient uptake by plants. So, there is a need to study the effect of herbicide on nutrient uptake by plants. The present study was undertaken to investigate the effect of atrazine, a widely used herbicide, on the uptake of nutrients by sorghum seedlings.

In view of very little research work on atrazine in soils of Karnataka state, Present investigation was undertaken with the following objectives:

1. To study the extent of adsorption of atrazine in selected soils of Karnataka (Ullal, Kemmannagundi and Dharwad).

2. To study the extent of adsorption of atrazine in these soils as influenced by the addition of organic matter which is a common practice to stabilise the fertility and to increase the productivity of soils.

3. To study the extent of persistence of atrazine as influenced by alternate wetting and drying processes in the above soils.

4. To study the kinetics of degradation of atrazine in these soils.

5. To study the uptake of nutrients by sorghum seedlings in presence of atrazine in Dharwad black soil.

REVIEW OF LITERATURE

II. REVIEW OF LITERATURE

Increased interest in the use of herbicides was initiated with the invention of 2,4-D (2,4-Dichlorophenoxy acetic acid) and its use as selective herbicide. Since then, a modern era in chemical weed control started. Since world was II and particularly, after the invention of high yielding varieties, there has been an increased usage of organic pesticides in various segments of our environment.

With the advent of chemical weed control in agriculture, there has been increasing awareness of the importance of soil colloids in the adsorption, movement, persistence, degradation and bioactivity of these herbicides. The problems of phytotoxicity of these herbicide residues in food and fodders and detoxification of these herbicides as a result of herbicides soil colloid interaction are of major importance to agriculturists, consumers, pollution control agencies, public health organisations and several others. As such, findings of many studies carried out in several countries are available in the literature. However, only the very relevent and important information on the adsorption and persistence of atrazine a well known chloro s-triazine herbicides, in soils and factors affecting these processes are reviewed below.

According to Bailey and White (1970), seven factors are known to influence the fate and behaviour of pesticides in soil systems, namely chemical decomposition, photo-decomposition, microbial decomposition, volatilization, movement, plant or organism uptake and adsorption. The phenomenon of adsorption and desorption directly or indirectly influences the magnitudes of the effect of other factors. Adsorption, therefore appears to be one of the major factors affecting the interactions occuring between pesticides and the soil colloids.

2.1 Adsorption of triazines by soils

The literature on adsorption of triazine herbicides in soil and on soil components and related materials are voluminous. Literature citations in this review are limited to studies that appears to be significant in natural soil systems recognizing their complexities.

2.1.1 Effect of soil properties on adsorption

The process of herbicide adsorption involves an interaction between the electrical charges on the herbicide molecules and the soil surfaces. The phenomenon is regulated by characteristics of the soil solution. The way in which soil components are responsible for the adsorption depends upon the physical and chemical properties of both soil and the adsorbate. The extent of adsorption are determined by the soil colloids including the nature and amount of clays, organic matter, exchangeable bases etc.

The properties of the adsorbate determining adsorption on soil colloids are (a) chemical characterstics, shape and configuration (b) acidity or basicity of the molecule (PK_a or PK_b), (c) water solubility (d) charge distribution on the organic molecule (e) polarity (f) polarizability and (g) molecular size (Bailey and White, 1970; Morril et al. 1982).

Soil is peculiar in having both seperate basic and acidic constitutents. The basic ones are comparatively less in number, electric charges are less on them and have smaller surface. They consist mainly of hydrated aluminium and ferric oxides, the latter are particularly potential adsorbers of anions, (Mithyantha, 1973). Soil is an excellent adsorbent for retaining both organic and inorganic compounds too (Edwards, 1975). The major adsorption surfaces in soils are on clay particles and organic matter (Ketchersid and Merkle, 1975; Kliger and Yaran, 1975 and Wu et al., 1975). Since organic matter and clay do not exist as seperate entities in soil, it is often impossible to know which soil component in the adsorption processes plays important role.

As mentioned above, the amount of an organic compound adsorbed on soil, depends on number of adsorption sites and is usually a function of specific surface and charge density (Morill *et al.*, 1982). To sum up, the adsorption of a given triazine herbicide is largely affected by the physico-chemical characteristics of the soils, of these organic matter content, nature and amount of clay minerals and exchangeable cations deserve consideration.

1. Soil organic matter : There are many evidences to show that, for most toxicants, soil organic matter is primarily responsible for sorption (Hayes, 1970; and Morill *et al.*, 1982). Soil organic matter is a complex mixture ranging from relatively undecomposed plant and animal remains to complex polymeric humic materials arising from microbial or chemical degradation processes (Burns *et al.*, 1973). Soil organic matter has a high cation exchange capacity and the total CEC of the soil mostly depends upon the soil organic matter content.

Hayes (1970) reported that because of variations in composition of organic colloids in soil, the adsorption of organic molecules on soil particles varies from soil to soil. Hence, eventhough organic matter plays an important role in the adsorption of organic molecules, it can rarely be used alone for predictive purposes. The mineral organic matter interactions determine the adsorptive capacity of each soil (Saltzman et al., 1972; Meggit, 1970).

It is widely believed that the soil could reduce the phytotoxicity of triazines including atrazine, by adsorbing the chemical. Upchurch et al. (1966) observed that organic matter content was the single soil factor which was closely related to the GR_{50} values of several herbicides. Similar results were also reported by Day et al. (1968). Streibig (1979) worked on the effect of soil characteristics like texture, exchangeable bases and acidity on the extent of Kd values i.e. the ratio between herbicide concentration adsorbed to the soil and left in the soil solution and GR_{50} value i.e. the herbicide concentration in PPmw required for soil to reduce dry matter production to 50 per cent and found that correlation existed between Kd and GR_{50}. These were also correlated to CEC, exchangeable bases and organic matter content. The dissipation rate and adsorption of atrazine were related with organic carbon content, but no correlation between either dissipation rate or adsorption and clay content. The extent by which triazine herbicides were adsorbed on Fenland muck soil (79 per cent O.M. and 10 per cent cation sites saturated with hydrogen ion) decreased in the order prometryne $>$ propazine $>$ atrazine(Hayes et al., 1968).

The manner in which a herbicide reacts with the different soil organic matter fractions like humic acid, fulvic acid and humin is important from the herbicides organic matter interaction point of view, in any perticular soil. Triazines have been shown not to be adsorbed by soil polysaccharides and by the brown fulvic acid materials extracted from a muck soil with dilute H_2SO_4 (Hayes et al. 1968). McGlamery and Slife (1966), showed that humic acid adsorbed more atrazine at pH 2.5 than at pH 7.0. Hayes et al. (1968) reported that atrazine propazine, norazine, desmetryne and prometryne were adsorbed strongly on to hydrogen ion (H^+), Calcium ion (Ca^{++}) and Barium ion (Ba^{++}) saturated humid acid and humin preparations.

2. Soil clay : Next to organic matter, mineral clays are the important adsorbents of added toxicants in soils particularly in the tropics where soil organic matter content is low, clays are considered to be the summum bonum of soils. They give the soil its CEC, high surface area and are responsible for adsorption. Generally, adsorption is positively correlated with clay content, though this is governed by the nature of clays.

Frissel (1961) reported that adsorption of herbicides on clays are much sound and systematic on the basis of both theory and experiments. He worked with suspension of a 2 /U fraction of three different clay minerals like illite, montmorillonite and kaolite. He observed the extent of adsorption of triazines including atrazine. He concluded that these were adsorbed by clays, the kaolinite has the least adsorptive capacity among the three minerals since it has the smallest surface area. Among different types of clays, the expanding (2:1) minerals such as montmorillonite and vermiculite have higher CEC and high surface area (80-150 me/100g CEC and 600 to 800 sq.m/g surface area). They gives rise to the coulombic forces and Vander Waal's forces and consequently impart a considerable adsorption capacity. Non expanding types of clays such as mica, kaolinite and chlorite, because of their low CEC and low surface area, do not have as large adsorption capacity as montmorillonite and vermiculite (Bailey and White, 1970).

Adsorption of organic compounds (herbicides) by clay minerals differs because of CEC, the strength of negative charges, the specificity of adsorption sites and the nature of the cation on the exchange complex (Mithyantha et al., 1975).

Terce and Calvet (1978) reported that montmorillonite had a greater adsorption capacity than illite or kaolinite, in general. But they concluded that, with atrazine, no clear relationship between adsorption and clay properties could be established and reported that probably the adsorption of atrazine was mainly due to the surface impurities such as the Al or Fe oxides/hydroxides.

Normally, 1:1 type clays possess a very low net negative charges. The 2:1 type of clays carry high net negative charge due to isomorphic substitution of Al^{2+} or Fe^{3+} for Si^{4+} in the tetrahedral layer and/or Mg^{2+} or Fe^{2+} for Al^{3+} in the octahedral layer. These negative charges comprise the CEC and are balanced by closely adhering cations. Filep et al. (1979) reported that the degree of atrazine adsorption was influenced mainly by the quality of organic and mineral colloids contents, pH value of the soil and the adsorptive energies of soils. Smith et al. (1980) reported that adsorption of atrazine occured on amorphous components of soil colloids, resulting in the lesser availability to plants and for degradation.

In view of the large quantities of herbicides getting adsorbed in soils and thereby becoming unavailable, it is necessary to estimate, the optimum quantities of herbicides to be applied to different soils by studying their adsorption capacities.

3. Exchangeable cations: Exchangeable cations either directly or indirectly affect the adsorption of organics in soils. There exists considerable differences between different cations to exchange for another cations from exchange site. Evidences are also ample depicting the differences among cations to replace the adsorbed organic molecules.

Nearpass (1967) observed a decrease in the adsorption of simazine and atrazine in a clay soil with increase in the base saturation, irrespective of the nature of saturating cations and the decrease was thought to be due to occupation of adsorption sites by cations, rather than specific effects of the bases. Adsorbed cations alter the pH of the soil and hence the adsorption is also affected. Some of the polyvalent metal cations like Ca^{2+}, Mg^{2+}, Al^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+} and Ce^{4+} help to form co-ordinate bond between clay surface and pesticide molecule (Greenland, 1965). Coordination has been shown to be an important mechanism for adsorption of a variety of pesticides on clay surface and the strength of adsorption is governed by the nature of cation (Bailey, 1971). Some cations like Na^{+} brings about dispersion of clay, thus increasing the surface area available for adsorption.

Gaillardon (1975) worked on the influence of pH on the adsorption of atrazine by humic acid of soil and the competitive effect of cations like Ca^{2+}, Al^{3+} and Fe^{3+}. He concluded that protonated form of atrazine can be adsorbed by ion exchange mechanism. Calcium shows a weak capacity for displacement in relation to the adsorbed atrazine.

Harris and Hurle (1978) working with K-montmorillonite or Na-Bentonite clay, concluded that, lowering of solution pH through plant activity resulted in increased adsorption of atrazine.

Skipper _et al_. (1978) reported that when montomorillonite and allophanic clay were staurated with H^+, Al^{3+}, Cu^{2+} and Ca^{2+}, the H^+ and Al^{3+} saturated montmorillonite clay promoted the hydrolysis of atrazine, while Ca^{2+} and Cu^{2+} saturated clay did not. But allophanic clay did not catalyse the hydrolysis of atrazine when saturated with H^+, Al^{3+}, Ca^{2+} or Cu^{2+}. More over, they also concluded that allophane was not sufficiently acidic to protonate the atrazine.

Smith _et al_.(1981) reported that the addition of anions (½ PO_4, $C_6H_5O_7^{3-}$, VO_3^- and OH^-) supressed the adsorption of atrazine in some South African soils. According to Terce (1983) the adsorption isotherms obtained for the adsorption of a weak organic base atrazine ($PK_{(b)}H^+ = 1.68$) by kaolinite and montmorillonite were different according the clay suspension dilution, whatever may be the compensating cations (Na^+, Ca^{2+} or Al^{3+}).

4. Soil reaction: Adsorption studies with well characterised minerals have shown the dependence of the extent of adsorption on pH for many herbicides. Frissel (1961) and Frissel and Bolt (1962) found that the adsorption of herbicides with widely different molecular structures increased as the pH of the medium decreased. The pH where maximum adsorption occured was dependent on the compound and adsorbent. The action of solute, solvent and adsorbing surface may be pH dependent. The maximum adsorption of many organic compound reportedly occur when pH = pKa where the two forms are of equal concentrations. Bailey *et al.* (1968) found that regardless of the chemical character of the adsorbate, adsorption occured to the greatest extent on the highly acid hydrogen montmorillonite (pH 3.35) compared to the near neutral sodium montmorillonite (pH 6.8). They also concluded that the magnitude of adsorption of organic compounds with widely different chemical character is governed by three factors, such as pH of clay suspension, water solubility and the dissociation constant of the adsorbate.

Stefanovite and Tomko (1976) reported that, pH affected both solubility and adsorption of atrazine. The amount of atrazine retained by the soil was inversely proportional to the pH (Hiltbold and Buchanan, 1977).

5. <u>Temperature</u>: Adsorption process are exothermic and desorption process are endothermic in nature and an increase in temperature would normally be expected to reduce adsorption and favour the desorption process. This corresponds to a weakening of the attractive forces between the solute and the solid surface and between adjacent adsorbed solute molecules with increasing temperature and corresponding increase in solubility of the solute in the solvent (Bailey and White, 1970). Similar results were reported by Dao and Lavy (1978). According to Harris and Warren (1964), adsorption of simazine, atrazine and monuron by bentonite was greater at 0°C than at 50°C. Increase in the temperature increases the solubility of the compound and thus reduces its adsorption (Goring, 1967). Increase in temperature increases the vapour pressure of atrazine there by reduces the adsorption. Atrazine loss essentially doubled with 10°C increase in temperature as per Kearney <u>et al</u>. (1964). However, there are some conflicting reports to the above general trends. Dao (1977) reported that atrazine adsorption in soil was increased when there is increase in soil temperature from 5°C to 30°C.

2.1.2 Adsorption as effected by adsorbate characteristics

Characteristics of herbicides such as solubility, molecular weight, functional groups, charge distribution, polarity and molecular configuration have been found to affect the degree and amount of adsorption on solid surface (Haque and Freed,1974).

Ionic or induced charge property of organic compounds is also known to influence the extent of adsorption (Adams, 1973). Charge can be strong if there is equal distribution of electrons and can be weak if there is unequal distribution of electrons in the molecule. Polarity expressed as the dipole movement of compounds is considered to favour the adsorption on surfaces according to Mills and Bigger (1969). The polarity of the molecule will also influence the degree to which it is solvated in solution which in turn will influence the over all energy required for adsorption. The realtive polarity of solute, adsorbent and the solvent would appear quite important in determining the extent of overall adsorption reaction as per Bailey and White (1970).

Adsorption is said to decrease as solubility in the solvent increases (Bailey et al., 1968). Ashton (1961) showed that mobility of triazine herbicides increased in the order of their solubilities. As the water solubility decreases an increase in the hydrophobic character of pesticides occur resulting in the increased adsorption by soil clays and organic matter as reported by Colemen and Thomas (1967). But Webber (1970a) reported that solubility differences of s-triazines were not reflected in differences of adsorption. Formulation or the form in which pesticides are applied affect their solubility and adsorption. Generally, water soluble ~~form~~ are adsorbed less than the oil soluble and water immiscible forms (Edwards, 1964). Emulsions were more readily adsorbed than wettable powders or miscible liquids, presumably due to the higher solubility of latter formulations.

Size, structure and stability of the molecule also affect the adsorption. Adsorption decreased with an increase in molecular size of adsorbates as a result of pore size limitations in the adsorbent according to Morril et al. (1982). Molecular size will have an effect on the magnitude of adsorption and on the ability of organics to be adsorbed on internal surfaces by high layer charge clay, e.g. vermiculite. If a large ion can cover more than one electrostatic exchange site (e.g. exchange site area for montmorillonite is approximately 80°A), the result will be an over all decrease in the adsorption capacity of the mineral (Bailey and White, 1970).

Stability of adsorbate is important when soil adsorption is measured by the concentration difference technique. Any undetected decomposition of adsorbate will lead to over estimation of adsorption. The extent of adsorption and the ease of desorption are influenced by the pH of the compound in the aqueous solution. Since the possibility of adsorption of an organic compound is high when the soil pH is near the pKa or pKb of the compound (Bailey and White, 1964 and Adams, 1973).

2.1.3 Mechanisms of adsorption

Of late, more and more adsorption studies with pesticides are being conducted on an intensive scale all over the world. The excellent theoretical treaty given by Frissel (1961) sets a high standard of excellence on the subject. He described the principle underlaying sorption of neutral and charged organic molecules on various types of clays. Accordingly adsorption of a given compound may occur due to one or a combination of different mechanisms viz., physical adsorption, chemical adsorption including ion exchange and protonation, hydrogen bonding and co-ordination.

According to Bailey and White (1970), several mechanisms or combination of mechanisms can be postulated for adsorption of organic compounds of aluminosilicates. Some of these are (1) physical adsorption i.e., adsorption due to Vandeer Waal's forces (a summation of dipole-dipole interactions, dipole induced dipole interactions) and ion dipole (2)hydrggen bonding (3) coordination complexes and (4) chemical adsorption.

Physical adsorption involves Vander Walls forces which result from short range dipole-dipole interactions of several kinds. The dispersion interaction (induced dipole) appears to be the most important factor in determining the Vander Walls forces for simple molecules. Due to the complex nature of the soil colloid, cation - water system it is not feasible to study the individual interactions which are responsible for Vander Waals forces. Physical adsorption or Vander Waals adsorption results from electrostatic interactions between atoms, ions and molecules due to electron fluctuations that produce instantaneous dipoles. The energy of adsorption due to Vander Waals interactions is low i.e. 1-2 cal/mol for atoms and small molecules which is only slightly greater than that of kinetic motion (0.6 cal/mol) at 25°C (Kiselev, 1965 and Watson, 1965).

Hydrogen bonding is a partial charge transfer interaction and is less energetic than coulombic interactions. The energy of adsorption in H-bonding systems may vary from

0.5 to 15 cal/mol. (Hadzi et al., 1968 and Hammaker and Thomson, 1972). Hydrogen bonding can occur on clay surfaces with the surface oxygen and protons of adsorbed water (Low 1961). Russell et al. (1968) reported that adsorption results from H-bonding between the adsorbent, carboxyl group and N-atom of the triazine ring which result in the protonation of a ring or side chain N-atom followed by cleavage of the C-Cl bond by water. Atrazine adsorption by humic acid was spontaneous. The humic acid-atrazine adsorption complex was thermodynamically stable. In the adsorption process, the change in entropy was positive and lay between 12.1 and 14.8 cal/mol per degree as reported by Khalebnikova and Konchints (1975). It is defficult to classify hydrogen bonding as physical adsorption or chemisorption. Hadzi et al. (1968), have suggested that there is a parallel between hydrogen bonding and protenation. Protonation may be considered as a full charge transfer from base (electron donor) to the acid (proton) electron acceptor and this bond is a partial charge transfer. For those organic compounds possessing a basic character and containing an N-H group, adsorption could occur by formation of a hydrogen bond between the amino group and the oxygen of the clay surface (Bailey and White, 1970). Chemical adsorption by soils and soil constituents can occur by at least four different mechanisms (1) ion exchange (2) protonation at the silicate surface or colloidal surface by reaction of the base with the hydronium ion on the exchange site (3) protonation in the solution phase with subsequent adsorption of the organic molecule via ion exchange (4) protonation by reaction with the dissociated protons from residual water present on the surface in systems having water of hydration or in co-ordination with the exchangeable cation Bailey and White, 1970).

The pesticides which are weak bases (including atrazine) and exist as cations and their exchange with metal ions on clay will depend on their ability to accept a proton from the medium which in turn is determined by the pH. Thus, the surface acidity of clay minerals may provide the source of H^+ for protonating pesticides. These protons may exist on the exchange sites of clay minerals or may be generated from water associated with exchangeable metal ions (Mortland, 1968). Russel et al. (1968) reported that some s-triazines were shown to become protonated at clay mineral surfaces. Webber (1966) demonstrated, for a series of s-triazines, that maximum adsorption on montmorillonite occured at a point in the vicinity of the pKa value of each compound. A further lowering of the pH resulted in some desorption of s-triazones which was attributed to the competition of the protonated species with H^+. An alternate explanation would be that, the low pH released Al^{3+} from the clay lattice which would be a stronger competitor than H^+ to displace the protonated molecule.

Co-ordination is an important mechanism in the adsorption of non ionic polar organic compounds. The co-ordination number is the number of ligands complexed around the metal and is a function of the metallic ion and the ligand configuration and is less common to s-triazines. But adsorption due to co-ordination of linuron and atrazine to organic matter through Ca^{2+}, Ni^{2+}, Ca^{2+}, Fe^{3+} and Ce^{4+} is also shown to occur (Hance, 1971).

Atrazine adsorption by humic acid was shown to be governed by two fixation mechanisms arising from interaction either with π electron carried by the adsorbent and adsorbate or between ionized carboxylic functional group and the proton of N-H bonds. According to Chassin et al. (1981), these interactions help in explaining the influence of atrazine molecular structure and/or the physcial, chemical state of the adsorbent on the level of adsorption. Besides this, complex formation is also suggested to be a possible mechanism of adsorption of atrazine in some South African soils as per Smith (1981). Terce (1983) reported that the adsorption of atrazine is by the molecular protonation near the surface of clay colloid followed by coulombic interaction between the organic cation and the variable negative charge of kaolinite or montmorillonite.

The energy of adsorption or strength with which the adsorbate is held may be regarded as the summation of the effects of these different forces acting between the adsorbent and the adsorbate. Generally, physical adsorption results in the low heat of sorption or low binding strength while chemical adsorption gives high heat of adsorption or high binding strength. In the physical adsorption, several layers may be present but in the case of chemical sorption, although several layers may be present, only the first layer is chemically bonded to the surface and others are held by dipolar attraction and inter molecular forces.

2.1.4 Methods of study of adsorption

Various approaches have been used to gain insight into the effects of the nature of the colloid on the adsorption of herbicides by soils. Two indirect lines of approach that have been used are (1) assessment of the effect of soil type and organic matter content on the resultant bioactivity of the compound in question since it is assumed that the degree of reduction of bioactivity is due largely to adsorption and (2) determination of the leachability of a herbicides as a function of soil type and organic matter content. The direct approach has been, to determine adsorption isotherms using soil colloids. All these methods have been used by several research workers.

The effect of soil type and organic matter content on the bioactivity of pesticides has been assessed by determining the percentage control at a given dose or comparing the differences in the dosage required to effect a given per cent control. This approach has been extensively used for herbicides (Ashton, 1961; Sheet, 1970). The leachability of pesticides as a function of their bio-activity has been studied by Upchurch and Pierce (1957 and 1958). But the direct approach has been largely used at present for almost all pesticides (Bailey et al., 1968). The data on the adsorption isotherm are fitted in several model equations such as Freundlich, Langmuir or BET (Bailey et al., 1968).

An adsorption isotherm is obtained by plotting the amount of substance (adsorbate) adsorbed on a solid (adsorbent) against the amount remaining in the solution at constant temperature and the graph represents equilli-brium conditions (Gills, 1970). According to Burns et al. (1973) the difference in time required to reach equillibrium reflect molecular complexities of adsorbates and adsorption surfaces. Adsorption varies widely as the soil to solution ratio is altered (Hance, 1970).

According to Gills et al. (1960) the particular type of adsorption isotherm originates due to specific interaction between the adsorbate molecules and the adsorption sites.

They classified adsorption isotherms into four basic types namely S, L, C and H types. S-type of curve is obtained if the solute molecule is mono functional or has strong intermolecular attraction with in the adsorbed layer and/or the solvent is strongly adsorbed. L-type also known as Langmuir type curve is found where there is no strong competition from the solvent for sorption sites on the solid surface or if the adsorbate has linear or plannar molecules and the major axis is parallel to the adsorbent surface. C-type of curve is characterised by constant partition of adsorbate between solution and adsorbent. The C-type is found mainly with textile fibers where the adsorbate penetrates the fibers as the concentration in the solution is increased. Linearity of C-type shows that the number of sites for adsorption remains constant i.e. as more solute is adsorbed more sites become available. The linear isotherms also suggesting a partition between solution and the Stern layer of the adsorbent. H-type is obtained in systems with a high affinity between the adsorbate and adsorbent. Such a curve can result from chemisorption or adsorption of ionic miceles or polymeric molecules. The initial part of the plot is therefore essentially vertical.

The L-type of isotherm has been observed for the adsorption of s-triazines by non-montmorillonite (Webber, 1966 and Bailey et al., 1968). Bailey et al. (1968) also found that the adsorption isotherms were well described by the use of Freundlich equation but did not confirm well to Langmuir equation. The Freundlich equation is an analytical expression for general parabola and theoreticaly adsorption increases indefinitely with increasing concentration, but this is ideally suited for beterogenous systems like soil-water-pesticide systems (Furmide and Osgenby, 1967). The Langmuir equation is an expression of a reactangular hyperbola passing through the origin and tends to attain a definite limit for the adsorption of adsorbate on the surface. The Langmuir equation was developed for adsorption of gases on solids and has a sound conceptual basis but is not as successful in predicting adsorption from liquid solution as for gases on surface and is useful only when multilayer adsorption is not involved. When Langmuir equation fails to explain adequately the experimental adsorption data, the Freundlich equation might be used which is emperical and can be derived from surface free energy and Gibb's adsorption equation for dilute solutions. Neither the Freundlich nor the Langmuir equation provides for a within on curve maximum and break down at high solute concentrations (Brash and Layman, 1971). In the field conditions the heterogenity of adsorbents may reduce the usefulness of the Freundlich and Langmuir equations to merely emperical description.

As the assumptions in the development of Langmuir equation are restricted to mono molecular layer adsorption, more complicated theories and isotherms have been developed for explaining the multilayer adsorption, which includes Brunsauer, Emett and Teller (BET) equation. The BET equation has been used for studying the adsorption of pesticides which are having high vapour pressures. However, in a soil system adsorption from solution is of primary concern (Matsumura, 1975).

In addition to the adsorption isotherms, the distribution coefficient (Kd) values are calculated to predict the quantity of added herbicide remaining in the solution and the quantity adsorbed, Nearpass (1967) used this concept for herbicides like Amitrole and s-triazines. He defined the Kd value as the ratio of the quantity of a compound adsorbed per unit weight of adsorbate to the equillibrium concentration. He also concluded that his concept can be extended to all the other pesticides.

Whatever may be the way in which adsorption expressed, it is the energy of adsorption that is important. The partial molal free energy ΔG defined by $\Delta G = -RT/nKd$ is often used as a measure of the driving force for adsorption reaction (Bailey and White, 1968). However, to know fully the characteristic adsorption of a toxicant on a given soil, it is necessary to know the enthalpy and entropy changes as a result of adsorption. While, enthalpy change indicates the strength of binding, the entropy refers to the order or degree attained. Even the attempts were made by Mills and Biggar (1969) to develop an equation for finding out the isoelectric heat of adsorption based on Clausius-Clapeyron equation. The isoelectric heat of adsorption is defined as the differential heat of adsorption when the amount of adsorbate is kept constant.

2.2 Persistence and degradation of triazines in soils

Herbicides remain toxic in soil for varying periods of time. In general, organo chlorine pesticides are the most persistent since they are least readily degraded. The longer the persistence the greater the probability that the pesticides will find its way into ground water (Morill *et al.*, 1982).

Persistence in soils has been defined by Hill and McCarty (1967), as the length of time that a pesticide takes to decompose 75 to 100 per cent of the original compound. Kearney *et al.* (1969) defined it as the time required to reduce the pesticidal concentration to 75 or 100 per cent of the amount initially added. Hiltbold (1974) presented a broader definition of persistence as the period during which a chemical remains intact and biologically active.

In terms of environmental pollution another term "terminal residues" has been associated with persistence of pesticides (Edwards, 1971). Terminal residues have been defined as metabolic products with toxicities equal to or higher than the original compound. They also have more stability and persistence than the original, compound (Matsumura, 1972).

The s-triazines herbicides exhibit varying degree of persistence in soil. Disappearence rate are dependent on several environmental and edaphic factors. Some of these compounds persists in the soil for longer time than the other and the time required to degrade them is dependent upon the soil conditions and the nature of the compound. The process of adsorption influence and regulates the rate of decomposition of pesticides in soils. Generally, adsorbed chemical is not available for degradation. Even the pesticides have been shown not to move readily through soil profile since they are held in place or retarded by adsorption on organic matter and clay minerals. Those that persist for several years may pollute shallow ground water through slow elution or with other organic compounds (Morill _et al_., 1982). Persistence of atrazine and simazine as well as improper application can cause problems. This has been recognised when crops were grown in rotation with corn(Anon., 1970). Herbicides persistence in soil is drastically reduced by run off and varies with the kind of herbicides and among compounds with in a group having allied chemical structure. Generally s-triazine herbicides with a methoxy substitutent in the two position of the ring are more persistent than those containing the methylthio substitutents as per Sheet et al. (1962).

Once a pesticide is applied to the soil a dynamic equillibrium is established between its adsorbed and solution phase and as the pesticide molecule is removed by decomposition, leaching or uptake by the plant. Desorption from the adsorbed phase occurs to reestablish the equillibrium. According to Furmidge and Osgerby (1967), this is explained by the relationship:

$$\text{Soil-pesticide adsorption complex} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{pesticide in solution} \xrightarrow{k} \text{decompsotion}^{2} \text{ products.}$$

The rate constant for the decomposition 'k_2' is dependent on the soil type and its value is same within a soil as that in an aqueous solution at the same pH and temperature if the degradation is only chemical. The rate constant for adsorption, k_1 is assumed to be very large while that for the desorption, k_1 is assumed to be very much greater than k_2. Thus in principle it should be possible to calculate the persistence of the herbicide if the soil adsorption constants, Freundlich's 'k' and 'n' and the rate constant are known. Switzer and Rauser (1960) ranked the triazines in the order of activity and persistence in soil as simazine $\geq$ atrazine $>$ propazine $>$ ipazine trietazine $>$ chlorozine. Mithyanatha (1973), reported that the order of persistence of atrazine in four soils were Karl $>$ Black $>$ Laterite $>$ Red.

The half life concept has often been employed to compare the differences in the persistence between the several pesticides in a given soil environment. Half life is a measure of the time required for a pesticide to drop to half of the original concentration. Although this concept is useful in comparing the persistence of related compounds, it assumes that the rate of decomposition is logarithemic.

$$t_{\frac{1}{2}} = \frac{\ln^2}{k}$$

This is the equation used for calculation of half life of pesticides and in case of first order kinetics it is clear that it is dependent on initial concentration (Hamaker, 1972).

Russel *et al.* (1968) reported that persistence of pesticides in soil could be estimated from the hydrolytic half life time only in the pH regions where these compounds were also sensitive to chemical hydrolysis. In general, the rate of hydrolysis increased in the presence of soil as a result of a catalyzing effect of the soil in their breakdown. When half lives in soil of the triazine herbicides were compared with the adsorption constants, a functional relationship was observed in soils, as the adsorption is increased the halflife in the soil also increased. Swain (1969) reported that dissipation rate of atrazine followed first order kinetics with half life of 70 days in clay loam soil and this rate of dissipation did not differ significantly between application rates. Pestemer et al. (1983) worked on the persistence of simazine and atrazine in the loamy soil at 3 sites of Rumania. They reported that the time for 50 per cent loss of atrazine varies from 36 to 68 days.

The kinetics of pesticide degradation reaction must be considered in order to be able to estimate the availability of a pesticide molecule for decomposition. While it is difficult to predict the order of the reaction for the decomposition of the selected pesticides in a soil water system, evidence has been given that the degradation of majority of the pesticides seems to obey first order kineties under natural conditions. A first order kinetics which can be expressed as exponential function is

$$C = C_0^{e^{-kt}}$$

By applying logarithem, the relation for first order kinetics is reduced to

$$\log C = \log C_o - 2.303\, kt.$$

where 'c' is the concentration of pesticide at time 't', C_o is the initial pesticide concentration and 'k' is the degradation rate constant. The value of k is shown to be negatively correlated and bears a definite relationship with the half life of the pesticide in the environment (King and Mc carty, 1968).

Several factors influencing the reaction kinetics involved in the biochemical degradation of pesticides in soil have been cited. These are concentration, temperature, moisture content, time and soil properties. Hamaker (1972), Kaufman and Kearney (1976) added two more factors namely, previous applications of the same compounds and their analogues or isomeric compounds and biological population dyanamics.

Reaction kinetics of biological and chemical decomposition of pesticides are concerned primarily with the decline in the concentration of the pesticides with in a period of time (Hamaker and Thompson, 1972 and Hance, 1979). Hamaker et al.(1966) proposed the 'rate law' and 'reaction rate modelling' concepts of pesticide biodegradation in soil. The rate of degradation was significantly and negatively correlated with soil pH. With atrazine the rate constant varied faster in summer and slower in early rainfall as per Nearpass *et al.* (1978). Swain (1979) reported that the dissipation rate of atrazine follows first order kinetics and the rate of dissipation did not differ significantly between application rates.

2.2.1 The degradation process

Degradation of pesticides in soils is to a large degree mediated by microbes but do occur non biologically like photo and chemical degradations. But of these, chemical and microbial degradations are important. Soil microorganisms may act upon pesticides in several ways. One mechanism may involve degradation with ultimate detoxication of the chemical, whereas, another mechanism may involves the activation or toxication of an initially non-toxic pesticide molecules. Still another mechanism may involve the transformation of toxic molecule into a product which exerts some beneficial influence upon higher plants, soil fauna and flora. Because of the public health and environmental significance of pesticide and their residues proper understanding of chemical, physical and microbial forces acting upon these chemicals are important. In soils both chemical and microbiological processess operate simultaneously (Pionke and Chesters, 1973).

2.2.2 Factors influencing the degradation of pesticides in soils

Several factors influence the degradation of pesticides and other organic compounds in soils. The factors that influence the chemical degradation of organic compounds in soil are (1) chemical structure of the compound itself (2) organic matter content of soil (3) pH of the soil (4) other compounds or ions present (5) concentration of the added compound and residues from earlier application (6) amount and kind of clay minerals in the soil (7) formulation of the compound and (8) application method (Morill *et al*., 1982). The environmental components that affects pesticide degradation in soils are (1) moisture (2) temperature (3) aeration and (4) depth of application.

Among these, the effect of soil type and moisture content are most important and they only are reviewed here.

2.2.3 Effect of soil type on degradation

The degradation process of pesticides is influenced by the properties of soil. This may be direct or indirect. It is direct in the soil where the pH and the quality of its microflora determines the rate of decomposition. It is indirect where the soil properties such as nature and amount of clay and organic matter affect the adsorption of added pesticides. The adsorption controls the rate of decomposition. The concentration of pesticide remaining in the solution which is available for decomposition is greatly affected by the degree and tenacity of adsorption (Anon, 1968). Strongly adsorbed toxicants decompose slowly but their persistence increased. Obien and Green (1969) observed that soil pH and organic matter content largely control the rate of degradation. They also concluded for soils with similar pH, atrazine degradation rates decreased with increase in organic matter content.

Agnihotri et al.(1976) concluded that atrazine degradation was maximum in acid soil, intermediate in alkali soil and lowest in the neutral soils. Citric acid and oxalic acid treatments were very effective in accelerating atrazine degradation. Ammonium sulphate and urea slightly enhanced the atrazine degradation in acid soil and suppressed in alkaline soils. Acetic acid and phosphoric acid treatment were effective only in alkaline soil. Treatment with IDET-20 (surfactant) increased the persistence of atrazine in all soils.

Hiltbold and Buchanan(1977) reported that the persistence period of atrazine in soils mainly depends on soil type, pH and atrazine concentration. Persistence increased with increase in pH. Rahman et al. (1977) reported that the residual activity of atrazine was increased significantly as a result of both moderate and heavy compaction treatments of soils. Terce et al. (1977), concluded that clay minerals are unlikely to play an important role in the degradation of atrazine except perhaps in the upper layer of soil during summer. Swain (1979) concluded that dissipation rate of atrazine was correlated with organic carbon content of soil but there was no correlation between dissipation rate and clay content.

Nikas Burkhard and Guth (1980) reported that the rate of triazines degradation was generally faster in the presence of soil which has obviously catalyzed the hydrolysis of atrazine at acidic pH. Smith et al.(1980) reported that an increase in pH increased the persistence of atrazine whereas increase in P-level decreased the persistence of atrazine. They also reported that some adsorbed atrazine was not available for degradation. Liming the highly acidic soils released adsorbed atrazine.

Rhode et al. (1981) reported that persistence of atrazine in surface 10cm of soil was more, than at the greater depth. They also concluded that the persistence did not very significantly with application rate.

2.2.4 Effect of moisture content on degradation

The relation of triazine persistence (or conversely decomposition) to soil properties like soil temperature and moisture can be best assessed where the conditions can be controlled. So, mostly laboratory experiments are to be done to asses the effect of these factors according to Burnside (1961). The soil environment into which herbicides are introduced determines to a large extent the rate of disappearance and many differences in persistence among soils can surely be attributed to variations of temperature and moisture.

Wilson and Cole (1964) compared the effect of three watering schemes on the persistence of atrazine. Persistence was greatest in soil that was watered to field capacity once each weak, intermediately persistent in soil that was watered to field capacity every 3.5 days and least persistent in soils that was watered daily to field capacity. These result indicate that moist conditions enhanced the degradation and decreased the persistence. The dry period decreases the degradation and increases the persistence, since soil moisture influences the activity of soil microorganisms that degrade the herbicides. Harris (1967), reported that weather and climate alter persistence through their effect on degradation (photo chemical, biological and non biological decomposition).

Microbial decomposition depends on favourable temperature and mositure conditions and non biological decomposition is also dependent on moisture and temperature. Warm moist climate promotes disappearence of triazine herbicides and the persistence is prolonged in cold dry climate (Harris, 1967; Harris et al., 1969 and Burnside, 1968). Harris et al. (1969) also concluded that non biological decomposition might be slow if soils are extremly dry.

Hamilton and Arle (1972) stated that the relatively longer persistence of herbicides in desert lands is due to low moisture. The degradation of atrazine to hydroxy atrazine by hydrolysis was dependent on soil type, atrazine concentration and moisture content (Skipper and Volk, 1972).

Lebedeva and Shustrova (1975) showed that triazine residues persisted in the order simazine > atrazine > prometryne. The detoxification was faster in cropped than in non cropped soil, in moist than in the dry soil, in long cultivated soil than in soils more recently brought into cultivation.

The chemical hydrolysis and microbial breakdown of pesticide in soils are dependent upon the moisture content; the rate of breakdown or hydrolysis being faster at higher moisture content. However, higher the moisture content higher the microbial activity. The chemical effect of moisture on hydrolysis of pesticides and other organic compounds in soils is chiefly due to the solution and dispersion action of the compound. The physical effect is due to its capacity to displace organic compounds from adsorption sites releasing the compound into the soil solution. According Morill et al.(1982), degradation rate of atrazine increased with increase in moisture upto the level just below the saturation point. But, Walker (1978) reported that atrazine degradation was least dependent on soil moisture.

2.3 Nutrient uptake in presence of triazines

The desire for quick and easy method of killing the unwanted plants (weeds) has given rise to a large number of chemicals that are known as weed killers or herbicides. The vast usage of these brought a major revolution in agriculture and horticulture practices. But plant being a delicately balanced organism any single change will have multiple effect. The target effects of these chemicals on weeds have been investigated but their side effects on the economic plants, especially on the nutrient uptake is very important. Barber (1976), reported that ion uptake capabilities of the root is one of the parameter affecting the efficiency with which a plant can recover nutrients from the soil. Therefore any agricultural practice interfering with the uptake process can influence fertilizer efficiency. Since, weed control by herbicides has become one of the major practice in agriculture, the question arises wheather this practice can effect the adsorption of nutrients by its effect on the biochemical systems of the plants. A brief review on the effect of triazines on nutrient uptake by crop plants are given below.

Herbicides are known to inhibit the metabolic processes like respiration, electron transport, photosynthesis (Hill's reaction), nucleic acid and protein synthesis. These are also known to alter the lipid metabolism resulting variation in the nutrient uptake (Audus, 1976). There are many evidences to show that s-triazine group of herbicides are known to inhibit the Hill reaction during photosynthesis. Atrazine is known to inhibit RNA, protein and lipid synthesis as reported by Ashton and Crafts (1973). Further, it has been recently reported that atrazine can effect the transport of nutrients in the roots through the plasma membrane (Renosto *et al.* , 1979).

Frency (1965) reported that very low concentration of simazine can increase the uptake of all the nutrients by corn seedlings under solution culture. He found that there is an increase in N uptake upto 37 per cent over the control. He also reported that application of simazine at the rate of 1.5ppm to soil increased the N uptake upto 29.5 per cent over the control and there was an increase in P uptake by 25 per cent over control by corn treated with simazine. He also noticed an increase in the uptake of potassium by 41 per cent and magnesium content by 24 per cent.

Ries et al. (1967) reported that triazines at sub-lethal concentration increases the N and protein content in different plant species. They worked on the effect of sub-lethal doses of simazine on rye and pea seedlings, and they reported rye seedlings had 45 per cent more water soluble protein per plant than in the corresponding control plants. They also reported an increase in protein contents of several crops including beans, peas, rice, rye grass and alfalfa as a result of simazine application.

Dhillon et al. (1967) reported in their incubation studies that uptake of phosphorus by seedlings from a nutrient medium containing 0.0015 ppm p^{32} was stimulated by 5 to 10 ppm of simazine. According to them, the increase in P uptake at low concentration of simazine may result in growth promotion and at higher concentration, growth depression and cause injury.

Polugar (1969) reported that atrazine at 1 to 4 kg/ha applied as pre emergence application increased the phosphorus and potassium contents of leaves and seeds of field beans. Singh *et al*. (1969) reported that greater uptake of N by corn seedlings from culture medium containing different levels of simazine. When they used 1 kg a.i./ha, nitrogen per cent of corn grain increased from 2.63 (control) to 3.61 (treated), but at the higher rates of application i.e. 2 kg a.i./ha, N per cent decreased from 2.63 to 2.45. Similar trend were noticed for atrazine also.

Chopra *et al*. (1970) observed an increase in the nitrogen content of groundnut leaves 15 and 75 days after the application of simazine. They did not notice any disturbance in the phosphorus uptake in groundnut. Hiranpandit (1972 and 1975) reported that sub lethal or low levels of atrazine increased the uptake of Ca by 13.8 per cent more than the control. They also noticed that an increase in potassium uptake from 5.75 (control) to 6.20 when treated with 1.5 ppm atrazine. The per cent phosphorus increase was from 0.47 in control to 0.51 in 3 ppm atrazine treated corn seedlings.

The application of atrazine, simazine and cynazine increased the nitrogen contents of herbage by 29, 23 and 14 per cent respectively, indicating that atrazine significantly influenced the uptake of nitrogen (Anon., 1975). Joshi and Datta (1976) reported that application of simazine at the rate of 1 kg a.i./ha and above showed an increase in the uptake of nutrients both in maize and wheat.

Renosto et al. (1979) found that the treatment with 10^{-4}M atrazine to roots of maize, barley and wheat inhibited the sulphate uptake capacity. Chopra et al. (1970) noticed an increase in sulphur content in groundnut by the application of simazine.

Suseela Devi (1979) reported that the application of simazine increased the per cent of N, Cu and soluble protein in corn seeds. A significant increase in the amount of total phosphorus in corn leaves and inorganic P in corn seeds were noticed by application of simazine at 1.25 and 2.5 kg a.i./ha respectively. Uptake and distribution of potassium was not affected. Increase in the uptake of calcium was observed and it was uniformly distributed among the different parts of plants, whereeas Mg distribution was very much affected by herbicide treatment rather than uptake. Higher concentration of simazine inhibited the uptake of iron by corn plants whereeas magnesium absorption was increased. Simazine at 0.625 kg a.i./ha resulted in the accumulation of Cu in corn seeds.

Pawa and Prakash (1980) reported that the prometryne and atrazine applied at 5-100 mg as premergence application to the surface of 1 kg soil/pot reduced the germination, root and shoot lengths and also dry weight of pea seedlings but found more nitrogen and phosphorus contents in the treated seedlings than the untreated. Giadina et al. (1983) worked on the action of atrazine and its biodegradation products on the membrane transport of potassium in roots. They reported that atrazine and deethylated atrazine inhibited the K^+ transport interacting directly with the plant cell membrane withOout distinguishing between resistant and sensitive plants.

Channabasavegowda (1986) reported that corn plant showed an increase in fresh and dry weights with atrazine, however with addition of organic matter this stimulatory effect of herbicide was reduced. Nitrogen per cent in corn plants increased significantly at the younger stages. No significant differences were seen in phosphorus content. Potassium content increased upto the recommended level and further there is no significant increase. No significant changes were noticed in calcium and magnesium contents at any growth stage, sulphur percentage increased with low level of 0.772 kg a.i./ha. Sinc and copper content increased significantly upto 1.562 kg a.i./ha. The manganese content in seedlings also increased under the influence of atrazine. He also concluded that, in general at recommended and below the recommended levels, the uptake of nutrients increased or remained unaffected with no adverse effect on plant growth.

MATERIAL AND METHODS

III. MATERIALS AND METHODS

The materials used and the techniques adopted during the course of investigation are described in this chapter.

3.0 Soil samples

For the purpose of present investigation, three important soils of Karnataka state viz. Black clay soil from Dharwad (Typic pellustat), Red acid soil from Kemmannagundi (Chickmagalore district, Oxic Rhodustalf) and Laterite sandy loam from Ullal (South Kenara district, Ustoxic distropept) were selected. Samples were collected from spots which had no known history of herbicide application. These samples were brought to the laboratory, dried in shade, powdered, passed through 2mm sieve and stored in the plastic bread boxes. The general characteristics of these soils are presented in the Table 1.

3.1 Methods of soil analysis

3.1.1 Physical properties of soils

1. Mechanical analysis: The per cent of coarse sand, fine sand, silt and clay present in different soils were found out by hydrometer method as outlined by Jackson (1967).

2. Maximum water holding capacity: Water holding capacity of soils was measured by Keen Raczoski method (Piper, 1966).

3. Field capacity: A 500 ml measuring cylinder was packed with soil uniformly by gently tapping and adding soil. Then about 250 ml of distilled water was added to this cylinder without disturbing the packed soil and kept over night after covering the cylinder with polythene sheet. After 24 hours, soil sample was collected from top 2 cm of the soil column. Then the moisture content was determined by drying in hot air oven, which was maintained at 105°C for 8-10 hours.

3.1.2 Chemical properties of soils

1. pH : The pH of the soil was determined in 1:2.5 soil water suspension using a glass electrode pH meter (Type CL49, Toshniwal company).

2. Electrical conductivity: The Electrical conductivity of soil was measured in 1:2.5 soil water extract using conductivity bridge type CM82T, Elico model.

3. Organic carbon and organic matter: Organic carbon was determined by Walkley and Black's wet oxidation method making use of the heat of dilution of sulphuric acid as

described by Piper (1966). The per cent of organic matter was obtained by multiplying per cent organic carbon by the factor 1.72.

4. Cation exchange capacity: Ten gram of soil sample was equilibriated and repeatedly leached with neutral normal ammonium acetate. The leachate, after making up the volume to 500 ml was used for the determination of exchangeable bases. The ammonia saturated soil was washed with isopropyl alcohol till the soil was free from electrolyte and the adsorbed NH_4^+ was replaced by K^+ by leaching again with 1N KCl and the leachate was made upto a known voluem. From this, an aliquot was used for the determination of ammonium by Macro Kjeldahls method. From the amount of NH_4^+ adsorbed, the CEC was calculated (Jackson, 1967).

5. Total exchangeable bases: An aliquot of ammonium acetate obtained under 4, was evaporated to dryness and ignited. The it was dissolved in 50ml of 0.5 N H_2SO_4. The excess acid was estimated by titrating against 0.05N NaOH with methyl red as indicator. Based on the amount of standard acid used, the total exchangeable bases were calculated.

6. Exchangeable Hydrogen: For the determination of exchangeable hydrogen, 10gm of soil sample was leached with 1N Barium acetate at pH 8.1. The leachate was titrated against standard NaOH solution (Jackson, 1967).

7. Available Nitrogen: Available nitrogen was determined by alkaline permaganate method as outlined by Jackson (1967).

8. Available Phosphorus: Olson's extractant was used for the black soil and Bray's extractant was used for the other two soils to extract available phosphorus. In the filtrate available phosphorus was determined by chloro-stannous reduced molybdo-phosphoric blue colour method in HCl system as per Jackson (1967).

9. Available potassium: Available potassium was extracted using neutral N ammonium acetate. The ratio of soil to extractant used was 1:5. In the ammonium acetate extract, potassium was determined flame photometrically.

10. Exchangeable calcium and magnesium: Exchangeable calcium and magnesium were extracted using neutral N ammonium acetate. In the ammonium acetate extract, exchangeable calcium and magnesium were determined by versenate titration method as outlined by Jackson (1967).

Table 1. Physical and chemical characteristics of the soils.

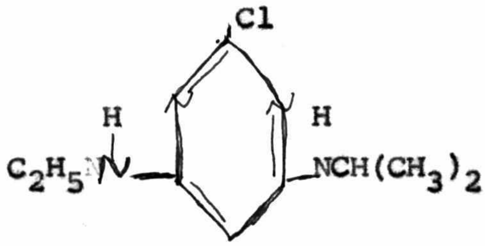
Sl. No.	Property	Ullal(S_1) soil (Ustoxic distropept)	Kemmanna-gundi(S_2) (Oxic Rhodstalf)	Dharwad (S_3) soil (Typic pellustat)
1.	Mechanical composition			
	Coarse sand (%)	62.5	7.1	7.9
	Fine sand (%)	29.2	56.1	24.1
	Silt (%)	8.0	14.0	22.0
	Clay(%)	10.0	22.0	46.0
2.	Textural class	Loamy sand	Sandy clay	Clay loam
3.	Maximum water holding capacity (%)	23.2	39.4	52.21
4.	Field capacity(1/3 bar tension)	17.0	27.0	36.00
5.	pH	4.4	6.7	7.30
6.	E.C.(mmhos/cms at 25°C)	0.078	1.55	1.725
7.	Organic carbon (%)	0.83	0.61	0.54
8.	CEC (me/100g)	17.8	20.1	52.5
9.	Dominent clay mineral	Kaolinite	Amorphous	Montmorillo-nite
10.	Available N (kg/ha)	113.2	200.9	145.2
11.	Available P (kg/ha)	2.1	10.5	2.3
12.	Available K (kg/ha)	105.0	40.0	102.0
13.	Total exchangeable bases (me/100g)	5.1	8.5	30.5
14.	Base saturation (%)	28.65	42.29	58.10
15.	Exchangeable Ca (me/100g)	2.2	5.0	23.0
16.	Exchangeable Mg (me/100g)	1.4	1.2	5.5
17.	Exchangeable H^+ (me/100g)	8.0	7.0	1.5
18.	Organic matter (%)	1.43	1.05	0.93

3.2 Adsorption studies

3.2.1 Nature of herbicide used

The herbicide used for the study was of analytical grade. Atrazine (2 chloro, 4-ethyl amino, 6-isopropyl amino s-triazine) was obtained from Rallies India Limited, Bangalore.

Structure



Properties

(1) White crystalline solid

(2) Melting point : 171-175°C

(3) Solubility: (a) Water = 23
(in ppm) (b) Organic solvent: 28,000

(4) Vapour pressure: mm Hg 293°K 3×10^{-7}

(5) Pk value = 1.68

(6) Dipole movement (Debyel constant) = 4.63

Common name : Atrazine,

Chemical Name: 2chloro-4 ethylamino 6 isopropyl amino s-triazine.

3.2.2 Preparation of adsorbents

For the adsorption studies natural soils (as given in 3) and soils amended with recommended level of well decomposed organic matter were used. The soils, after passing through 2mm sieve, were again made to pass through 0.5mm sieve.

One set of soils withoout additional organic matter and another set with additional organic matter were used for the study.

To understand the influence of clay minerals on adsorption, the dominent clay present in the soils were [redacted] determined. For this, clay fraction was seperated from soils. Samples are treated to remove calcium carbonate, organic matter, free iron oxides and amorphous oxides of aluminium and silicon. This step ensures that the mineral particles are dispersed and cleaned for satisfactory particle size fraction. Procedure adopted was as given by Jackson (1967). Identification of the dominent clay minerals in samples was made using X-ray diffraction technique. The X-ray diffraction analysis was carried out on Philips X-ray diffractometer, model PW 1050, with nickel filter, wave length 1.418 A°, chart speed 2cm/minute and Scan speed 2°/minute. The X-ray diffraction patterns were presented in the figure 1.

3.2.3 Determination of adsorption

1. Method of study: The method followed for the adsorption studies was essentially the same as described by Talbert and Fletchall (1965) with slight modification. One gram of sample of each soil was transfered to a series of clean

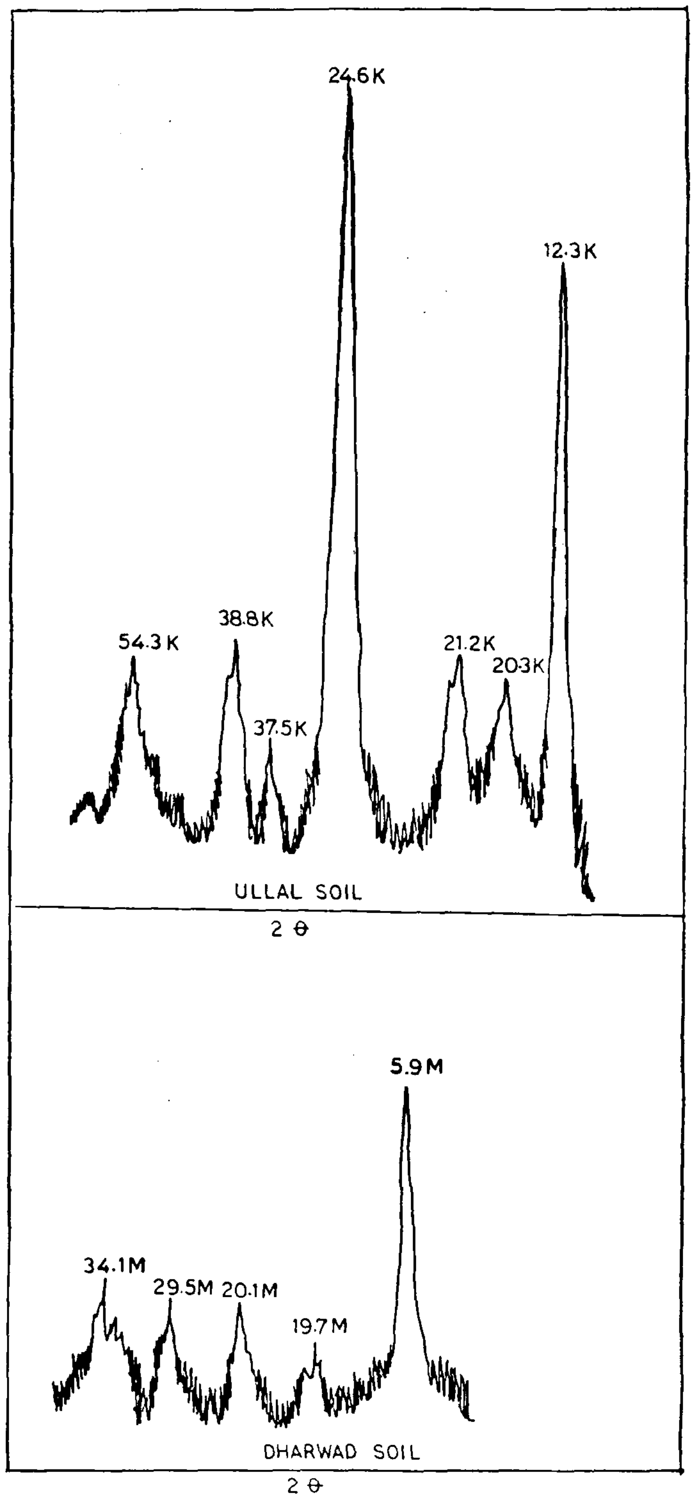


FIG.1: X-RAY DIFFRACTION PATTERN OF CLAY FRACTIONS OF TWO SOILS OF KARNATAKA.

100ml glass centrifuge tubes to which 1ml of 10 to 70 ppm atrazine solutions were added. Then the volume was made upto 25ml using distilled water. The samples used were natural soils and soils ammended with recommended dose of well decomposed organic matter as described above. Then, these tubes were shaken for 1 hour in a rotary shaker and kept overnight. After 24 hours, these tubes were shaken for 1 hour before centrifuging. The suspensions were centrifuged for 10-15 minutes at 1000 to 2000 r.p.m. with a pinch of barium chloride in order to get clear suspernatant. In the clear supernatant, the concentration of atrazine was determined at 240nm using u.v. spectrometer, Model 2005, Shimadzu make.

The quantity of atrazine adsorbed was calculated from the differences between the known amount of atrazine initially added and the quantity remaining in the equillibrium solution. This difference in concentration was assumed to be entirely due to adsorption.

2. Adsorption isotherms: From the data on the quantities of atrazine added, quantities adsorbed and the corresponding equillibrium concentrations, the adsorption isotherms were constructed. They were plotted as per Freundlich's adsorption equation since this could be applied to such heterogenous systems like soil pesticide water suspensions as:

$$X/m = KC^{1/n}$$

Where X/m = Quanatity of atrazine adsorbed per unit weight of soil ($\mu g/g$)

C = Equillibrium concentration in ppm

'K' and 'n' are constants.

The constants 'K' and 'n' were obtained respectively from the intercept and reciprocal of the slope of straight line graph obtained upon plotting the data on a log - log scale i.e.

$$\text{Log}\ (X/m) = \text{Log}\ K + (1/n)\ \text{Log}\ C$$

3.3 Persistence study

In the second part of the investigation, the persistence of atrazine was studied on all the three soils, as influenced by wetting and drying processes. Two levels of atrazine was used for the study.

3.3.1 Incubation procedure

Air dried sample of each soils were passed through 2mm sieve and 20g of soils were weighed into 50ml beakers. Then 10 and 20 μg atrazine were added and mixed well. Subsequently these soils were brought to field capacity by adding required quantity of distilled water. These were incubated at room temperature in the laboratory.

For each soil two sets of samples were set up, one for each concentration. The samples were drawn as per the schedule given below.

Sl.No.	Days after incubation		Wetting and drying cycles
1.	0	Ist cycle	At field capacity
2.	5		Drying period
3.	10		
4.	11	IInd cycle	Wetted to field capacity
5.	15		Drying period
6.	20		
7.	21	IIIrd cycle	Wetted to field capacity
8.	25		
9.	30		Drying period

At 0 day, the samples were brought to field capacity. Then the samples were allowed to dry upto 10th day. Again they were brought to field capacity on 11th day and allowed to dry upto 20th day, once again rewetted on the 21st day and again allowed to dry till 30th day. The atrazine remained in soils after degradation was extracted and determined at the intervals as shown above.

3.3.2 Method of atrazine residue extraction

The method of extraction for atrazine was essentially the same as given by Zweig (1964). The soil in each Beaker was successively extracted with 15ml portions of the solvent and the total volume of extract was made upto 100ml. Extraction was done in 125ml seperatory funnel. Details of extraction are given as under;

The soil sample was extracted repeatedly with 15 ml portion of dichloromethane (CH_2Cl_2) and the final volume of the extract was made upto 100ml. An aliquot of 25ml of this extract was transferred to 125ml separatory funnel, washed twice with 15ml portions of 2 per cent NaOH solution and 3 times with 15 ml portions of 0.5 N HCl. The washed CH_2Cl_2 extract was transferred to a beaker, evaporated to dryness on a waterbath maintained at about 55°C. The water extract of the residue, after making upto 25ml was used for atrazine determination (Zweig, 1964).

3.4 Uptake of nutrients

In the third part of the study, the uptake of nutrients by sorghum seedlings in presence of added atrazine was studied. The principle of the method employed was the one based on the original technique as described by Neubauer and Scheider (1923) with slight modifications. This was carried out only in black soil of Dharwad.

3.4.1 Method of study

Three 100 gm portion of air dry black soil of Dharwad which has been passed through a 2mm sieve were weighed out and each portion was mixed with 50gm of nutrient free acid washed quartz sand. This mixture was added to glass Neubauer dishes and spread uniformly, and moistened with 20ml of distilled water. Again another layer of 150gm of quartz sand was added and spread uniformly and moistened with 40ml of distilled water. A sampling board with 100 evenly distributed pegs was used to mark the surface of the sand and 100 carefully selected dry seeds of jowar (var. CHS-5) were dibbled into the sand. The seeds were covered with about 75 gms of dry quartz sand which was again moistened with 20ml of distilled water. Then different levels of atrazine herbicide solution were applied to the dishes. Three blanks were kept wherein herbicide was not added. These dishes are kept in the growth chamber covered with glass plate untill the seedlings touch the cover plates. At this point, cover plates are removed. The soils were brought to field capacity every day. At the end of the 17th day, seedlings in each dishes were counted and harvested separately.

The roots were washed with dilute HCl and then with distilled water so as to remove soil and sand. The dry weight and nutrient content of the seedlings in each dishes were determined. The uptake of nutrients by seedlings were then calculated.

3.4.2 Method of plant analysis

1. Collection and preparation of plant samples: The harvested and cleaned jowar seedlings were dried in an oven at 60-65°C for 6-8 hours. Then dried samples were powdered in a clean grinder fitted with stainless steel blades and preserved in polythene bags for further analysis.

2. Nitrogen content: For nitrogen determination, 0.5gm oven dry sample was digested in concentrated H_2SO_4 with K_2SO_4 + $CuSO_4$ + Se mixture as catalyst in Kjeldahl flask and distilled in the alkaline medium. The liberated ammonia was collected in 4 per cent Boric acid containing bromo cresol green-methyl red mixed indicator and titrating against standard acid. From the data, the per cent nitrogen was calculated (Jackson, 1973).

3. Digestion of plant samples for P, K, Ca and Mg : Accurately weighed 0.5g oven dry plant sample was disgested by wet oxidation method using triacid mixture (HNO_3, $HClO_4$, H_2SO_4 in the rate 10:4:1) in 100 ml Erlenmeyer flask as described by Piper(1966). This digest was used for the analysis of P, K, Ca and Mg.

4. Phosphorus: Phosphorus was determined by the vanado molybdate yellow colour method in HNO_3 medium. The colour intensity was read in the spectro photometer at 420mm wavelength as described by Piper (1966).

5. Potassium content: The potassium content in the digested sample was determined using flame photometer, (Piper ,(1966).

6. Calcium and magnesium: Calcium and magensium were determined by EDTA/versenate titration method (Piper, 1966).

Statistical analysis

Asymmetrical Factorial analysis was used to determine the superiority of soils in respect of adsorption, persistence and degradation of atrazine. To find out the Freundlich's constants 'k' and 'n' in adsorption isotherm studies, simple regression equation was worked out statistically.

In pot culture experiment, one way analysis was carried out to findout the effect of treatments.

EXPERIMENTAL RESULTS

IV. EXPERIMENTAL RESULTS

Three typical soils of Karnataka were selected to study the behaviour of atrazine in soils, like adsorption, persistence and also influence of this herbicide on nutrient uptake by plants. The soil selected were Ullal soil (Ustoxic distropept), Kemmannagundi soil (Oxic Rhodustalf) and Dharwad soil (Typic pellustat). The physical and chemical characteristics of these soils are given in the table 1. The Ullal soil was (S_1) loamy sand recording only 10 per cent clay. The pH of this soil was 4.4, organic carbon per cent was 0.83 and cation exchange capacity 17.8 me/100gm. The dominant clay was found to be (Fig 1), Kaolinite and per cent base saturation recorded was 28.65. The Kemmannagundi soil (S_2) was sandy clay recording 22 per cent of clay content, 0.61 per cent organic carbon and cation exchange capacity 20.1 me/100gm. Dominent clay mineral was mostly amorphous type since no characteristic crystalline structure, and per cent base saturation recorded was 42.29. The soil from Dharwad (S_3) was clay loam recording the highest clay content of 46 per cent. The pH of the soil was slightly alkaline (pH 7.9) and organic carbon per cent was 0.54. The cation exchange capacity recorded was 52.5 me/100gm and dominent clay mineral was montmorillonite (Fig 1). The per cent base saturation of this soil was found to be 58.1. The Ullal, Kemmannagundi and Dharwad soils will be hereafter referred as S_1, S_2 and S_3 respectively.

4.1 Adsorption of atrazine by soils

The data on adsorption of atrazine in 3 different soils taken for this present investigation are presented in tables 2, 3 and 4.

The data in table-2 are pertaining to Ullal soil (S_1). The quantity of adsorption increased with the increase in the concentration of initial quantity of the chemical. With 10/Ug/g of added atrazine, the quantity adsorbed was found to be 8/Ug/g in natural soil which increased to 9 /Ug/g in soil amended with organic matter. When the initial concentration of added atrazine was increased to 20 /Ug/g, the quantity adsorbed were 11 and 14 /Ug/g in natural and organic matter amended soil respectively. As furnished in the table 2, the quantity of adsorption in both natural and amended soils increased with increase in the initial concentration of atrazine, recording adsorption of 23 and 25 /Ug/g when the initial added concentration was 70 /Ug/g of soil.

Table 2. Adsorption of atrazine by Ullal (S_1) soil of Karnataka (Average of three replications)

Sl. No.	Quantity added µg/g	Quantity adsorbed (µg/g)	
		Natural soil	*Soil amended with organic matter.
1.	10	8(80.00)**	9(90.00)
2.	20	11(55.00)	14(70.00)
3.	30	14(46.62)	16(53.28)
4.	40	17(42.50)	18(45.00)
5.	50	19(38.00)	20(40.00)
6.	60	21(35.07)	22(36.74)
7.	70	23(32.89)	25(35.75)

S.Em± (Treatments)	0.4630
C.D. at 5%	1.3410
S.Em± (Soil type)	0.2475
C.D. at 5%	0.7168
S.Em± (Treatment x Soil)	0.6548
C.D. at 5%	NS
C.V. (%)	6.67

* Farm yard manure was applied at the rate of 10 t/ha

** Values in parantheses indicate the percent adsorption.

Obviously, the percentage of added atrazine adsorbed decreased from 80 to 32.89 per cent in natural soil corresponding to an initial concentration of 10 to 70 µg/g. However, when organic matter was added to the soil, per cent adsorption also increased with respect to all the concentrations. When atrazine was added at the rate of 10 µg/g, the per cent adsorption recorded in natural soil was 80 as compared to 90 per cent when soil was amended with organic matter with same initial concentration. Though, 10 per cent increase in adsorption observed with the addition of organic matter at this lowest concentration added atrazine, this difference was almost narrowing as the concentration of atrazine increased for instance, when atrazine, was added at the rate of 60 µg/g of soil, 35.07 per cent of added chemical was adsorbed on natural soil, whereas 36.74 per cent was adsorbed on organic matter amended soil.

The data on adsorption of atrazine by Kemmannagundi soil (S_2) are furnished in table 3. As the level of added atrazine increased from 10 µg to 70 µg/g of soil, the quantity of atrazine adsorbed ranged from 7.5 to 24 µg/g of soil. With every level of added atrazine, adsorption increased with the incorporation of organic matter. With the lowest level of atrazine

Table 3. Adsorption of atrazine by Kemmannagundi (S_2) soil of Karnataka (Average of three replications)

Sl. No.	Quantity added µg/g	Quantity adsorbed µg/g Natural soil	*Soil amended with organic matter
1.	10	7.5(75.00)**	9.0(90.00)
2.	20	10.0(50.00)	12.5(62.50)
3.	30	15.0(50.00)	17.0(56.67)
4.	40	17.0(42.50)	19.0(47.50)
5.	50	19.0(38.00)	21.0(42.00)
6.	60	22.0(36.74)	23.0(38.40)
7.	70	24.0(34.32)	25.0(35.75)

S.Em± (Treatment)	0.6569
C.D. at 5%	1.9026
S.Em± (Soil type)	0.3511
C.D. at 5%	1.0169
S.Em± (Treatment x Soil type)	0.9290
C.D. at 5%	NS
C.V. (%)	9.34

* Farm yard manure was applied at the rate of 10 t/ha.

** Values in parantheses indicates the percent adsorption.

(10 μg/g) , the quantity adsorbed was 9 μg/g in organic matter incorporated soil. As the concentration of added atrazine increased, the adsorption of atrazine also increased as in the case of natural soil.

The per cent adsorption in natural soil ranged from 75 to 34.32 corresponding to the initial quantity of added atrazine which varies from 10 to 70 μg/g soil. The per cent adsorption reduced consistently with increase in added quantity of atrazine. A similar trend was noticed when the soil was amended with organic matter too. The per cent adsorption varied from 90 to 35.75 as given in this table. When atrazine was added at the rate of 10 μg/g of soil, the per cent adsorption recorded was 75 in natural soil which increased by 15 per cent when the soil was incorporated with organic matter. At every level of added atrazine, the per cent adsorption was more in presence of added organic matter. However, as the initial concentration of atrazine increased, the per cent adsorption due to organic matter decreased.

The data on adsorption of atrazine by black soil of Dharwad (S_3) are presented in the table 4. The quantity of atrazine adsorbed ranged from 9 μg to 25 μg/g of soil, when the initial concentration of

Table 4. Adsorption of atrazine by Dharwad (S_3) soil of Karnataka (Average of three replications)

Sl. No.	Quantity added (µg/g)	Quantity adsorbed µg/g	
		Natural soil	*Soil amended with organic matter
1.	10	9(90.00)**	10.0(100.0)
2.	20	16(80.00)	18.5(92.50)
3.	30	20(66.60)	22.5(74.93)
4.	40	22(55.00)	25.0(62.50)
5.	50	23(46.00)	26.0(52.00)
6.	60	24(40.08)	27.0(45.09)
7.	70	25(35.75)	30.0(42.90)

S.Em± (Treatment)	0.5900
C.D. at 5%	1.7088
S.Em± (Soil type)	0.3153
C.D. at 5%	0.9134
S.Em± (Treatment x Soil type)	0.8343
C.D. at 5%	NS
C.V. (%)	6.78

* Farm yard manure was applied at the rate of 10 t/ha

** Values in parantheses indicate the percent adsorption.

atrazine ranged from 10 to 70 μg/g. When organic matter was incorporated with the soil, the quantity adsorbed ranged from 10 to 30 μg/g as the initial concentration ranged from 10 to 70 μg/g. In both natural and amended soil, the quantity of adsorption increased with the increase in concentration of added atrazine, though in soils with organic matter, adsorption of atrazine was more at every level of atrazine application. Ninety per cent adsorption was observed with initial atrazine concentration of 10 μg/g which decreased to 35.75 per cent as the added level of atrazine increased from 20 to 70 μg/g in natural soil. This per cent adsorption decreased consistently with increase in the concentration of atrazine. A similar trend was observed in soils amended with organic matter also. When soil was amended with organic matter, 100 per cent adsorption was noticed when the chemical was added at the rate of 10 μg/g of soil. However, per cent adsorption decreased to 92.5 as the initial concentration of atrazine was increased by another 10 μg. With further increase in the atrazine concentration, the per cent adsorption also decreased to a minimum of 42.9 with an initial concentration of 70 μg/g of soil.

When the per cent adsorption was compared between natural and amended soil, it was observed that at every

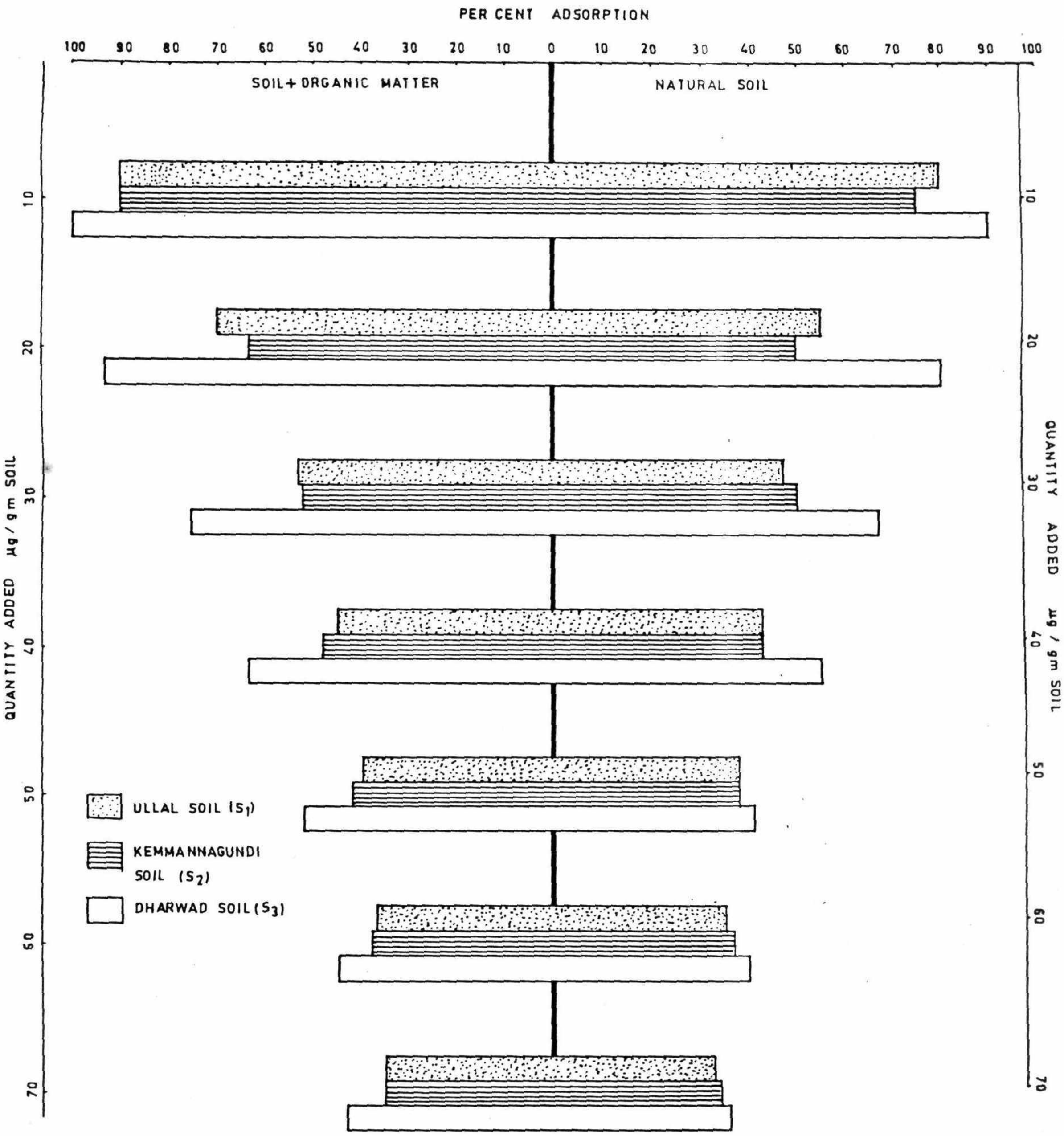


FIG. 2. ADSORPTION OF ATRAZINE IN SOIL

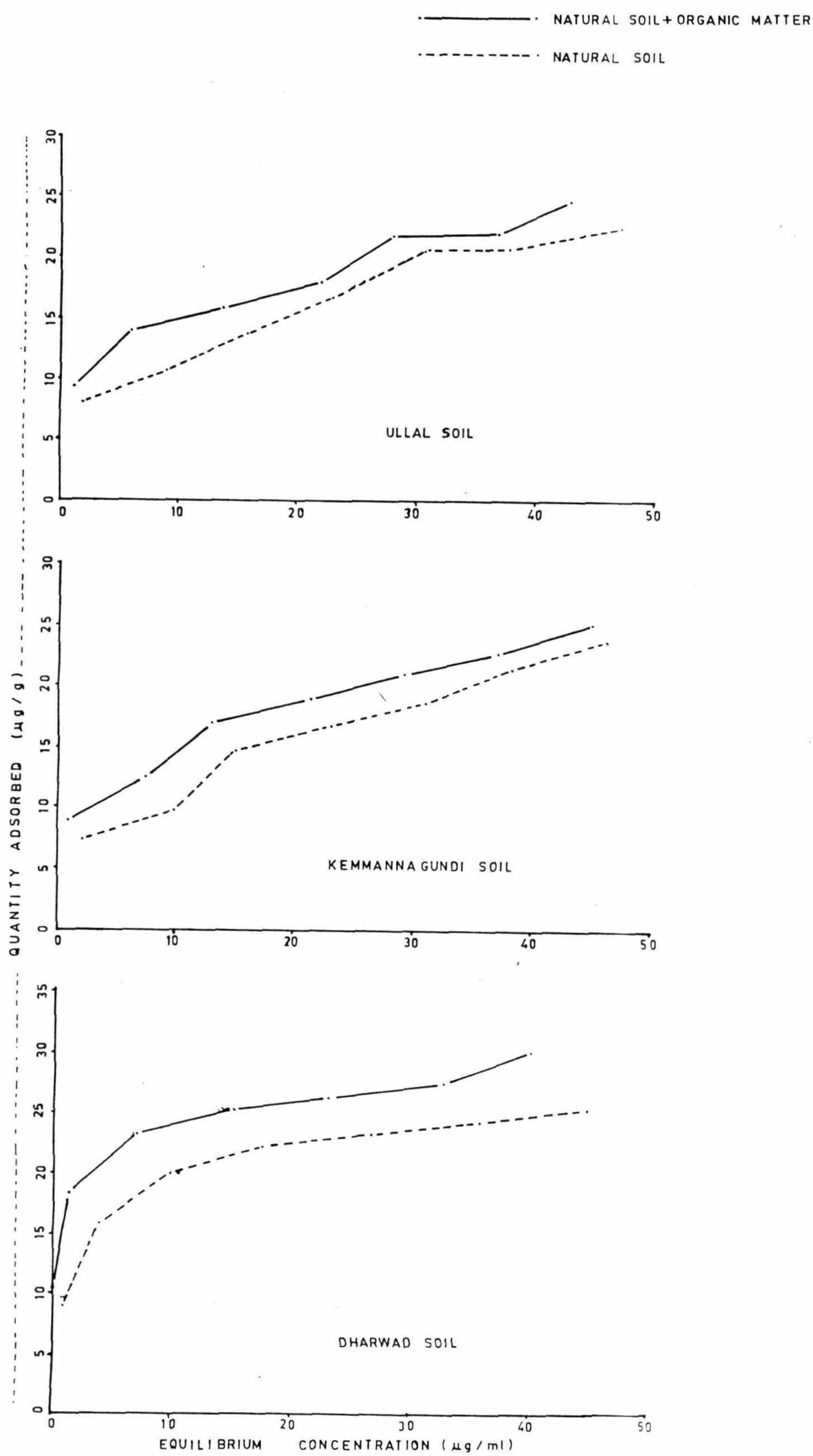


FIG.3: ADSORPTION ISOTHERMS FOR ATRAZINE.

level of added chemical the per cent adsorption increased in the presence of organic matter. The difference in adsorption due to organic matter narrowed down as the concentration of added atrazine increased.

The data of adsorption were treated using Freundlich's equation and the Freundlich's constants are given in the table 5. The values for constant K ranged from 4.71 to 10.04 in natural soil and 8.39 to 13.06 when soils were amended with organic matter. The lowest 'K' value (4.71) was found for soil S_2 and the highest was for soil S_3. The K value for S_1 soil was found to be 5.79. When organic matter was incorporated, S_2 recorded a K value of 8.39. The highest K value of 13.06 was found for soil S_3 with organic matter, where as the K value recorded in organic matter incorporated, Ullal soil (S_1) was 8.67.

For natural soil the value for constant 'n' ranged from 0.39 to 0.55, the lowest being for soil S_2 and the highest for soil S_3. The value for constant 'n' with respect to Ullal soil was 0.45. The values for 'n' increased when the soils were incorporated with organic matter. For soil S_3 the 'n' value recorded was 0.59 followed by 0.56 for S_1 and 0.54 for S_2.

Table 5. Adsorption of atrazine by soils (Freundlich's constants)

Sl. No.	Soils	Freundlich's constants			
		Natural soils		*Soils amended with organic matter	
		K	n	K	n
1.	S_1^{**}	5.79	0.45	8.67	0.56
2.	S_2	4.71	0.39	8.39	0.54
3.	S_3	10.04	0.55	13.06	0.59

K = Quantity adsorbed when its concentration in equillibrium is unity.

n = Measure the energy of adsorption

*Farm yard manure was applied at the rate of 10 t/ha

**S_1 = Ullal soil

S_2 = Kemmannagundi soil

S_3 = Dharwad soil

4.2 Persistence of atrazine in soils

Persistence of atrazine in three different soils viz., S_1, S_2 and S_3 as affected by wetting and drying are furnished in the table 6, 7 and 8 respectively.

The data on the persistence of atrazine in soil S_1 are presented in the table 6. The persistenc study was done using two initial concentrations of atrazine namely 10 μg and 20 μg/20g soil. At 0 day, when the soils were at field capacity, 95 per cent of added atrazine could be recovered with both the levels tried. At the end of the first drying cycle i.e. on 10th day, 85.5 per cent of added atrazine remained in soil corresponding to 8.55 μg out of 10 μg and 17.1 μg out of 20 μg per 20 gm soil. The rate of degradation was found same irrespective of the initial concentration of the chemical. On 11th day, when the soils were rewetted to field capacity, 20 per cent of the originally added (10 μg) atrazine degraded recovering only 80 per cent. Similarly, with 20 μg concentration, the per cent recovered on 11th day when the soils were at field capacity was 77 per cent. Then soils were allowed to dry after 11th day upto 20th day. Sampling was done on 15th day when the soils were in 2nd drying cycle. The per cent recovered was 75.5 per cent with 10 μg atrazine

Table 6. Persistence of atrazine in Ullal (S_1) soil as affected by wetting and drying (Quantity of atrazine added was 10 and 20 /ug/20gm of soil). (Average of four replications)

Sl. No.	Incubation period (days)	Quantity remained (/ug/20gm soil)	
		10 /ug atrazine	20 /ug atrazine
1.	0+	9.55(95.0)*	19.0(95.0)
2.	5	9.00(90.0)	17.7(88.5)
3.	10	8.55(85.5)	17.1(85.5)
4.	11+	8.00(80.0)	15.4(77.0)
5.	15	7.55(75.5)	14.2(71.0)
6.	20	7.00(70.0)	13.8(69.0)
7.	21+	6.70(67.0)	13.2(66.0)
8.	25	6.35(63.5)	12.0(60.0)
9.	30	5.95(59.5)	11.5(57.5)

S.Em± (Days)	0.1238	S.Em± (Levels x Days)	0.1751
C.D. at 5%	0.3427	C.D. at 5%	NS
S.Em± (Cycles)	0.12838	S.Em± (Days x Cycles)	0.2145
C.D. at 5%	0.3528	C.D. at 5%	NS
S.Em± (Levels)	0.1011	S.Em±(CyclesxLevels)	0.1751
C.D. at 5%	0.2880	C.D. at 5%	0.3527

S.Em± (Levels x Cycles x Days)	0.3033
C.D. at 5%	NS
C.V. (%)	5.3

+ Soil samples were at field capacity

* Values in parantheses indicates per cent recovery.

and 71 per cent with 20 μg of atrazine. By 20th day, 30 per cent of added atrazine degraded recovering only 70 per cent, when the initial concentration of atrazine was only 10 μg and with 20 μg of atrazine, 30.0 per cent degradation was recorded on 20th day recovering 13.8 μg out of added 20 μg. On 21 day, soils were again brought to field capacity. The per cent recovery came down to 67 per cent recovering only 6.7 μg out of 10 μg. The per cent recovery recorded on 30th day was 59.5 per cent with 10 μg of atrazine and 57.5 per cent with 20 μg level.

The quantity of recovery of added atrazine in terms of μg and also per cent recovery in soil S_2 are presented in the table 7.

During first sampling, 95.5 per cent of the added atrazine could be recovered when 10 μg per 20gm soil was incorporated. Soils were allowed to dry upto 10th day and the quantity remained estimated on 5th and 10th day. On 5th day, quantity remained was found to be 89.5 per cent which decreased to 85 per cent, on 11th day the degradation suddenly increased recovering only 77.5 per cent of the added atrazine. Again the soils were allowed to dry upto 20th day and at the end of this drying cycle, quantity

Table 7. Persistence of atrazine in Kemmannagundi(S_2) soil as affected by wetting and drying (Quantity of atrazine added was 10 and 20 μg/20 gm soil) (Average of four replications)

Sl. No.	Incubation period (days)	Quantity remained (μg/20gm of soil)	
		10 μg atrazine	20 μg atrazine
1.	0+	9.55(95.5)*	19.2(96.0)
2.	5	8.95(89.5)	17.6(88.0)
3.	10	8.50(85.0)	17.0(85.0)
4.	11+	7.75(77.5)	15.1(75.5)
5.	15	7.30(73.0)	14.4(72.0)
6.	20	6.40(64.0)	13.1(65.5)
7.	21+	6.00(60.0)	12.6(63.0)
8.	25	5.60(56.0)	11.4(57.0)
9.	30	5.30(53.0)	10.5(52.5)

S.Em± (Days)	0.0998	S.Em± (Levels x Days)	0.1411
C.D. at 5%	0.2843	C.D. at 5%	0.4021
S.Em± (Cycles)	0.0998	S.Em± (Days x Cycles)	0.1728
C.D. at 5%	0.2843	C.D. at 5%	NS
S.Em± (Levels)	0.0814	S.Em± (Cycles x Levels)	0.1411
C.D. at 5%	0.2322	C.D. at 5%	0.4021

S.Em± (Levels x Cycles x Days)	0.2444
C.D. at 5%	0.6966
C.V. (%)	4.4

+ Soil samples were at field capacity

* Values in parantheses indicates percent recovery.

recovered was 6.4 μg i.e. 64 per cent recovery. When the soil was rewetted on 21st day the recovery per cent suddenly decreased to 60 per cent. On 25th and 30th days, when the soils were in third drying cycle the quantity of atrazine remained were 5.6 and 5.3 μg respectively. Hence at the end of 3rd drying cycle, 53 per cent of atrazine remained on 30th day when the initial concentration of atrazine was 10 μg/20g soil. Similarly, 52.5 per cent could be recovered on 30th day when the quantity of atrazine incorporated was 20 μg/20gm of soil. The pattern of recovery was very much similar with both the levels of atrazine.

The persistence of atrazine in soil S_3 as affected by wetting and drying are given in the table 8. Ninety six per cent of the added atrazine was recovered on 0 day when soils were at field capacity at both concentrations of 10 and 20 μg/20g of soil. The quantity recovered was reduced to 92.5 per cent after 5 days which further reduced to 90 per cent on 10th day. On 11th day, soils were brought to field capacity. In the wet sample on 11th day, the recovery was 81.5 per cent which further reduced to 78.5 on 15th day and 75.5 per cent on 20th day. When the soil were wetted again on 21st day, the quantity recovered was 7.3 μg corresponding to 73 per cent recovery. The soils were further left to dry upto 30th day and at the end

Table 8. Persistence of atrazine in Dharwad (S_3) soil as affected by wetting and drying (Quantity of atrazine added was 10 and 20 µg/20 gm soil). (Average of four replications)

Sl. No.	Incubation period (days)	Quantity remained µg/20 gm of soil	
		10 µg atrazine	20 µg atrazine
1.	0+	9.60(96.0)*	19.2(96.0)
2.	5	9.25(92.5)	18.6(93.0)
3.	10	9.00(90.0)	18.0(90.0)
4.	11+	8.15(81.5)	16.4(82.0)
5.	15	7.85(78.5)	15.6(78.0)
6.	20	7.55(75.5)	15.2(76.0)
7.	21+	7.30(73.0)	14.6(73.0)
8.	25	7.00(70.0)	13.7(68.5)
9.	30	6.80(68.0)	13.0(65.0)

S.Em± (Days)	0.0460	S.Em± (levels x Days)	0.0650
C.D. at 5%	0.1313	C.D. at 5%	NS
S.Em± (Cycles)	0.0460	S.Em± (Days x Cycles)	0.079
C.D. at 5%	0.1313	C.D. at 5%	NS
S.Em± (Levels)	0.0376	S.Em± (Cycles x Levels)	0.065
C.D. at 5%	0.1072	C.D. at 5%	0.1857

S.Em± (Levels x Cycles x Days)	0.1129
C.D. at 5%	NS
C.V. (%)	1.878

\+ Soil samples were at field capacity

* Values in parantheses indicates percent recovery.

of this period 6.8 μg was recovered. When the per cent quantity remained was monitored in soils where the initial concentration of atrazine was 20 μg the pattern of recovery as a function of time was found to be similar as described above. With 20 μg, the per cent recovery on 30th day was 65 per cent corresponding to 13 μg out of the initially added 20 μg.

The persistence of atrazine as per cent degradation in three different soils are furnished in the tables 9, 10 and 11.

The data on per cent degradation of atrazine in soil S_1 are given in the table 9. The per cent degradation ranged from 5 to 40.5 when the initial concentration of atrazine added was 10 μg/20gm soil. The degradation consistently increased showing more degradation when soils were wetted to field capacity i.e. on 11th and 21st days as described earlier. Similarly, when the initial level was 20 μg, the per cent degradation ranged from 5.0 to 42.5. On 30th, day the per cent degradation was 40.5 and 42.5 when the levels of atrazine added was 10 and 20 μg respectively.

In soil S_2, the per cent quantity degraded ranged from 4.5 to 47.0 when initial concentration was 10 μg/20g soil.

Table 9. Degradation of atrazine in Ullal (S_1) soil as affected by wetting and drying (Quantity of atrazine added was 10 and 20 µg/20 gm of soil)

Sl. No.	Incubation period (days)	Degradation (µgms)	
		10 µg atrazine	20 µg atrazine
1.	0+	0.50(5.00)*	1.0(5.0)
2.	5	1.00(10.0)	2.3(11.5)
3.	10	1.45(14.5)	2.9(14.5)
4.	11+	2.00(20.0)	4.6(23.0)
5.	15	2.45(24.5)	5.9(29.0)
6.	20	3.00(30.0)	6.2(31.0)
7.	21+	3.30(33.0)	6.8(34.0)
8.	25	3.65(36.5)	8.0(40.0)
9.	30	4.05(40.5)	8.5(42.5)

S.Em± (Days)	0.0410	S.Em± (Levels x Days)	0.0580
C.D. at 5%	0.1168	C.D. at 5%	NS
S.Em± (Cycles)	0.0410	S.Em± (Days x Cycles)	0.0710
C.D. at 5%	0.1168	C.D. at 5%	0.2024
S.Em± (Levels)	0.0334	S.Em± (Cylces x Levels)	0.0580
C.D. at 5%	0.0954	C.D. at 5%	0.1653

S.Em± (Levels x Cycles x Days)	0.1004
C.D. at 5%	NS
C.V. (%)	5.3520

+ Soil samples were at field capacity

* Values in parantheses indicates percent degradation.

Table 10. Degradation of atrazine in Kemmannagundi (S_2) soil as affected by wetting and drying (Quantity of atrazine added was 10 and 20 µg/20gm of soil)

Sl. No.	Incubation period (days)	Degradation (µgm)	
		10 µg atrazine	20 µg atrazine
1.	0+	0.45(4.5)*	0.8(4.0)*
2.	5	1.05(10.5)	2.4(12.0)
3.	10	1.50(15.0)	3.0(15.0)
4.	11+	2.25(22.5)	4.9(24.5)
5.	15	2.70(27.0)	5.6(28.5)
6.	20	3.60(36.0)	6.9(34.5)
7.	21+	4.00(40.0)	7.4(37.0)
8.	25	4.40(44.0)	8.6(43.0)
9.	30	4.70(47.0)	9.5(47.5)

S.Em± (Days)	0.0489	S.Em± (Levels x Days)	0.0692
C.D. at 5%	0.1394	C.D. at 5%	0.1972
S.Em± (Cycles)	0.0489	S.Em± (Days x Cycles)	0.0847
C.D. at 5%	0.1394	C.D. at 5%	NS
S.Em± (Levels)	0.0399	S.Em± (Cycles x Levels)	0.0692
C.D. at 5%	0.1138	C.D. at 5%	0.1972

S.Em± (Levels x Cycles x Days)	0.1198
C.D. at 5%	NS
C.V. (%)	5.8628

+ Soil samples were at field capacity

* Values in parantheses indicates percent degradation.

Table 11. Percent degradation of atrazine in Dharwad (S_3) soil as affected by wetting and drying (Quantity of atrazine added was 10 and 20 /Ug/20gm of soil).

Sl. No.	Incubation period (days)	Degradation (/Ugm)	
		10 /Ug atrazine	20 /Ug atrazine
1.	0+	0.40(4.0)*	0.8(4.0)*
2.	5	0.75(7.5)	1.4(7.0)
3.	10	1.00(10.0)	2.0(10.0)
4.	11+	1.85(18.5)	3.6(18.0)
5.	15	2.15(21.5)	4.4(22.0)
6.	20	2.45(24.5)	4.8(24.0)
7.	21+	2.70(27.0)	5.4(27.0)
8.	25	3.00(30.0)	6.3(31.5)
9.	30	3.20(32.0)	7.0(35.0)

S.Em± (Days)	0.0387	S.Em± (Levels x Days)	0.0548
C.D. at 5%	0.1105	C.D. at 5%	0.1562
S.Em± (Cycles)	0.0387	S.Em± (Days x Cycles)	0.0671
C.D. at 5%	0.1105	C.D. at 5%	NS
S.Em± (Levels)	0.0316	S.Em±(Cycles x Levels)	0.0548
C.D. at 5%	0.0902	C.D. at 5%	0.1562

S.Em± (Levels x Cycles x Days)	0.095
C.D. at 5%	0.2706
C.V. (%)	6.4226

+ Soil samples were at field capacity

* Values in parantheses indicates percent degradation

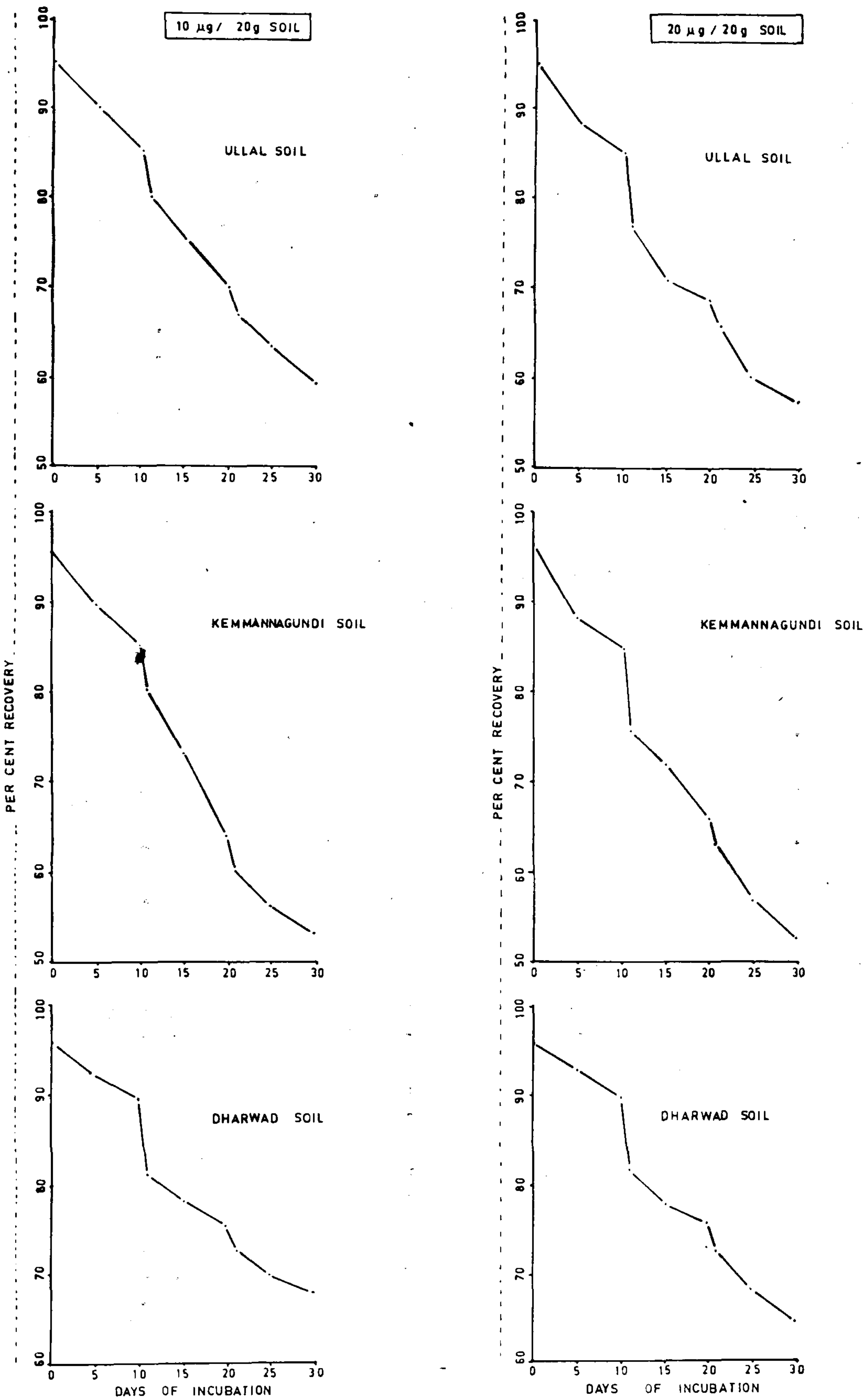


FIG.4: DISAPPEARANCE OF ATRAZINE IN SOILS

The soils were allowed to three drying cycles as discussed above. When the initial quantity of atrazine added was 20 μg, the per cent degradation ranged from 4.0 to 47.5 per cent as given in the table 10. The difference in the per cent quantity degraded between 10th and 11th day was 7.5 with 10 μg and 9.5 per cent with 20 μg. Similarly, on 21st day, 4 per cent of the original atrazine was degraded over that on 20th day with 10 μg/20gm of soil. Similar results was observed with higher level of atrazine.

The persistence of atrazine as per cent degradation in soil S_3 as affected by wetting and drying are furnished in the table 11. The per cent degradation ranged from 4.0 to 32.0 with 10 μg and from 4.0 to 35.0 per cent with 20 μg. On 10th day, 10 per cent degradation was recorded at both the levels of added atrazine, which increased to 18.5 and 18 per cent by wetting the soil on 11th day. Similarly, 2.5 and 3.0 per cent degradation of added atrazine was recorded on 21st day over that on 20th day at 10 and 20 μg levels respectively. On 30th day, the per cent degradation was 32 with lower atrazine level and it was 35 with higher atrazine level.

4.3 Uptake of nutrients by Neubauer technique

Atrazine was applied at four levels namely 0.0, 0.25, 0.5 and 1.0 kg a.i./ha to study the dry weight and also the nutrient uptake by sorghum seedlings from black soil of Dharwad by employing the principle of Neubauer technique.

4.3.1 Dry weight of sorghum seedlings

The dry weight of 17th day old sorghum seedling in black soil of Dharwad which was treated with different levels of atrazine are given in the table 12. The seedlings in control recorded a total dry weight of 2.57g which increased to 3.66 g amounting to an increase in dry weight by 42.41 per cent over the control with addition of 0.25 kg a.i./ha. With further increase in atrazine concentration to 0.5 kg a.i./ha the dry weight of seedling was 3.07 g amounting to 19.46 per cent increase over the control. However, when atrazine applied at the rate of 1.0 kg a.i./ha, the dry weight of sorghum seedlings further decreased to 2.81 gm amounting to 9.34 per cent increase over the control.

4.3.2. Nutrient content of sorghum seedlings

Nutrient content of sorghum seedlings as affected by atrazine in black soil of Dharwad are given in the table 13.

Table 12. Effect of atrazine on dry weight of 17 days old sorghum seedlings in black soil of Dharwad by Neubauer technique (Average of three replication).

Sl. No.	Treatments	Dry weight in g. (100 seedlings)	Percent increase in dry weight
1.	0.0 kg a.i./ha	2.57	-
2.	0.25 kg a.i./ha	3.66	42.41
3.	0.5 kg a.i./ha	3.07	19.46
4.	1.0 kg a.i./ha	2.81	09.34

S.Em± (Treatments) 0.02147
C.D. at 5% 0.7058

The per cent nitrogen in control seedlings was 2.91 which increased to 3.55 with atrazine at the rate of 0.25 kg a.i./ha. When atrazine level increased to 0.5 kg a.i./ha the per cent N decreased to 3.45, which further decreased to 3.15 with atrazine at the rate of 1.0 kg a.i./ha. A similar trend was noticed for phosphorus also. The phosphorus content ranged from 0.33 for control to 0.48 with atrazine at lowest level of 0.25 kg a.i./ha. With atrazine at the rate of 0.5 kg a.i./ha the per cent phosphorus recorded was 0.42 and with atrazine at the rate of 1.0 kg a.i./ha the per cent phosphorus recorded was 0.41.

The per cent content of potassium ranged from 1.33 to 1.81, the lowest being for control seedlings. With 0.25 kg a.i./ha the K per cent was 1.69 where as with 0.5 kg a.i./ha the highest potassium per cent (1.81) was noticed. By further increase in atrazine level, decreased the potassium per cent to 1.51.

The per cent content of calcium ranged from 0.81 to 1.31, the lowest being in seedlings which received atrazine at the rate of 0.25 kg a.i./ha. Increase in the atrazine concentration upto 0.5 kg a.i./ha, recorded a highest calcium content of 1.31 per cent. With further increase in atrazine level decreased the calcium content to 0.94 per cent.

Table 13. Effect of atrazine on nutrients content of 17 days old sorghum seedlings in black soil of Dharwad (S_3) vy Neubauer technique. (Average of three replications)

Treatments (Atrazine a.i./ha)	Nutrient content (%)				
	N	P	K	Ca	Mg
Control	2.91	0.33	1.33	1.00	0.73
0.25 kg a.i./ha	3.55	0.48	1.69	0.81	0.23
0.5 kg a.i./ha	3.45	0.42	1.81	1.31	0.35
1.0 kg a.i./ha	3.15	0.41	1.51	0.94	0.34

	S.Em± (Treatment)	C.D. at 5%
N	0.0456	0.1579
P	0.0119	0.0418
K	0.0005	0.0183
Ca	0.0715	0.02477
Mg	0.0007	0.0252

The per cent of magnesium was decreased with the application of herbicide. The highest per cent of magnesium was found in control seedlings i.e. 0.73 per cent. When the atrazine was added at the rate of 0.25 kg a.i./ha the per cent magnesium in seedling was only 0.23. However, the magnesium content significantly increased with the further increase in atrazine level.

4.3.3 Nutrient uptake by sorghum seedlings

The data on uptake of N, P, K, Ca and Mg by sorghum seedlings as affected by atrazine application in black soils of Dharwad are given in table 14.

The uptake of all these nutrients were low in control seedlings and the uptake increased with the application of herbicide. When the atrazine was applied at the rate of 0.25 kg a.i./ha, the maximum uptake of N was recorded as compared to other treatments. The uptake of N ranged from 74.79 to 129.93 mg/pot. The highest was recorded with lowest level of atrazine. With 0.5 kg a.i./ha, the N uptake was 105.91 mg/pot which decreased to 88.52 mg/pot with atrazine level @ 1.0 kg a.i./ha. Similarly, the seedling which recieved the atrazine at the rate of 0.25 kg a.i./ha, recorded a highest uptake of phosphorus (17.04 mg P/pot). As the level of atrazine

Table 14. Effect of atrazine on nutrient uptake of 17 days old sorghum seedlings in black soil of Dharwad by Neubauer technique. (Average of three replications)

Sl. No.	Treatments (Atrazine kg a.i./ha)	Uptake (mg/pot)				
		N	P	K	Ca	Mg
1.	Control	74.79	9.60	40.45	29.10	3.78
2.	0.25 kg a.i./ha	129.93	17.04	60.00	28.76	12.43
3.	0.5 kg a.i./ha	105.91	14.49	63.48	38.12	10.43
4.	1.0 kg a.i./ha	88.52	12.92	47.57	29.93	7.94

	S.Em± (Treatments)	C.D. at 5%
N	0.3061	1.4983
P	0.3202	1.1083
K	0.5380	1.8618
Ca	0.1911	0.9353
Mg	0.1820	0.6298

increased there was reduction in P uptake recording only 14.49 mg P/pot with 0.5 kg a.i./ha and 12.92 mg P/pot with 1.0 kg a.i./ha. The lowest P uptake was found in control seedlings.

Potassium uptake was favoured by lower levels of atrazine as shown in the table 4. Potassium uptake was increased when atrazine was applied at the rate of 0.5 kg a.i./ha (63.48 mg/pot); the next highest K uptake was noticed with 0.25 kg a.i;/ha corresponding to 60 mg K/pot. However, further increase in the rate of application of atrazine significantly decreased the K uptake to 47.5 mg K/pot. A lowest uptake of K (40.45 mg K/pot) was noticed in control seedlings.

The uptake of calcium was positively influenced by application of atrazine at the rate 0.5 kg a.i./ha which is the recommended level. The control seedling recorded an average uptake of 29.1 mg Ca/pot, which was almost on par with the calcium uptake by seedlings treated with 1.0 kg a.i./ha. However, atrazine at the rate of 0.25 kg a.i./ha recorded the lowest uptake of 28.76 mg Ca/pot.

When magensium uptake pattern was considered, application of herbicide favoured the uptake of magnesium.

The lowest level of atrazine application favoured the uptake of Mg to a great extent recording 12.43 mg/pot. However, this positive influence of Mg uptake reduced with increase in the levels of herbicides application. The control seedlings recorded only 3.78 mg Mg/pot which is significantly lower than for other treatments.

DISCUSSION

V. DISCUSSION

The discussion on the results of the investigation on adsorption and persistence of atrazine in three soils of Karnataka collected from Ullal (S_1), Kemmannagundi (S_2) and Dharwad (S_3) are furnished in this chapter. The uptake of nutrients by sorghum seedlings in the presence of different quantities of atrazine in Dharwad (S_3) soil was also studied and the results are discussed.

5.1 Adsorption of atrazine by soils

Adsorption of any organic molecule in the soils mainly depends upon the physico-chemical characteristics of the soil like organic matter, soil pH, moisture regime and exchangeable cations, etc. The data on the extent of adsorption of atrazine in different soils given in the preceding chapter reveal that a large quantity of added biocide is sorbed by the adsorbents. The adsorption data are best presented by adsorption isotherms and Freundlich equation was used to fit these isotherms in the present study. Although, Freundlich equation is empirical this can be used for explaining the adsorption of such compounds as pesticides on soils and this equation is best suited for such heterogenous systems like soil-pesticide-water systems (Graham Bryce, 1967; Bailey et al., 1968; Mills and Bigger, 1969). The Freundlich constant 'K' denotes the quantity of adsorbate adsorbed when its concentration in the equillibrium solution is at unity. The value of 'n' serves as a measures of the energy of adsorption (Bailey and White, 1970). In the present study the Freundlich equation has been employed mainly to find out the adsorbability based on the values of 'K'. This parameter is significant in deciding the amount of a given pesticide adsorbed in a ranges of doses applied to the agricultural soils.

According to Gills et al. (1960), a particular type of adsorption isotherm originates due to specific adsorption between adsorbate molecules and the adsorption sites. As per his system of classification of adsorption isotherms, the isotherm obtained in the present study is more or less near to the 'L' type which indicates that soils and organic molecule possess higher affinity for adsorption for atrazine. The 'L' type of isotherms have been considered to be most common occurring with many pesticides (Webber, 1970).

The data pertaining to adsorption of atrazine in different soils are furnished in tables 2 to 4 and illustrated in the fig.2. All the soils used in the present investigation showed higher affinity for atrazine. As the quantity of added chemical increased, the quantity adsorbed also increased, though, the per cent adsorption decreased based on the initial quantity of atrazine added in all the three soils. This may be due to lack of adsorption sites to synchronise with large quantity of added molecules as reported by many workers.

As shown in the fig.2, the black soil of Dharwad(S_3) recorded higher adsorption compared to other two soils. Higher adsorption by this soil may be due to higher amount of clay which was found to be of montmorillonite type (fig 1). This clay has higher surface area and exchangeable capacity. Clays are considered to be most important in adsorption and adsorption is reported to be positively correlated with clay content Liu et al., 1970; Mithyantha, 1973; Rajanna, 1983). Cationic organic chemicals and protonated species of basic organic chemicals are strongly adsorbed by clay minerals (Liu et al., 1971). Webber (1966) demonstrated for a series of s-triazines that the maximum adsorption on montmorillonite occurs in the pH in the viscinity of pKa value of each compound i.e. the pH at which the compound gets protonated. The studies of infrared spectrum made by Russel et al.(1968) and Webber (1970) conclusively proved that the principal mechanism of adsorption of atrazine on mineral colloids of soil is by protonation.

As illustrated in the fig.2, the addition of organic matter further increased the adsorption capacity of black soils of Dharwad. According to Hayes (1970), the herbicide may be adsorbed on organic matter due to Vander Waal's forces, hydrophobic bonding; ion exchange, charge transfer forces; ligand exchange or by chemisorption processes.

White and Cruz (1972) reported that the important properties of colloidal fractions of soil with regard to adsorption and related phenomenon are (1) the kind of the atoms constituting the surfaces (2) electrical properties and (3) intensity of charges. Organic soil colloids such as humic acid readily adsorbs cationic organic chemicals, basic chemicals and both polar and non-polar ionic species.

The influence of organic matter on adsorption of many herbicides was reported by many workers (Kearney et al., 1965; Harris and Sheets, 1965 and Sethi and Chopra, 1977). This high adsorption is facilitated by high surface area and high exchange capacity of organic colloids. According to Hamaker et al. (1966) unlike other adsorbents, organic colloids do not attain equillibrium very easily. A six fold increase in adsorption of atrazine was reported by Goring (1967), in humic acid when pH was lowered. According to Mithyantha (1973), Agnihotri et al. (1976) and Rajanna (1983), destruction of organic matter considerably decreased the adsorption of atrazine by soils.

The absolute quantity of atrazine adsorption was least in Kemmannagundi red soil than black soil of Dharwad. This can be explained not only on the basis of less amount of total clay but also its amorphous nature. In this soil, adsorption may be due to surface impurities of Fe/Al oxides and hydroxides. A similar trend was reported by many workers (Smith, 1978; Terce and Calvet, 1978).

The Ullal laterite soil (S_1) recorded more adsorption than that by Kemmannagundi red soil. This may be due to more native organic matter in soil S_1 than S_2 and the dominent clay was Kaolinite and pH was lower than in S_2 soil.

Liu et al. (1971) found that phytotoxicity of atrazine and related s-triazines are inversely related to the clay content as well as its cation exchange capacity. The ED_{50}

values of atrazine was directly related to the cation exchange capacity of several PeurtoRicon soils. Terce and Calvet (1978) observed that montmorillonite type of clay had greater adsorption capacity for herbicides than illite or kaolinite. This may be the most probable reason for higher adsorption in Dharwad (S_3) soil than Ullal and Kemmannagundi soils. However with the addition of organic matter to these soils, considerable increase in atrazine adsorption was observed. This confirms the findings of many workers (Harris and Sheet, 1965; Nearpass, 1965; Hayes, 1970; White and Cruz, 1972; Sethi and Chopra, 1977; Rajanna, 1983).

In the present study, soil mixed with organic matter generally adsorbed more amount of atrazine than the natural soils. Among the three soils studied, the Kemmannagundi red soil and Ullal laterite soil showed more adsorption capacity in presence of organic matter i.e. organic matter effect in these soils were more pronounced than in Dharwad black soil. These findings confirm that not only the amount and nature of clay but organic matter too substantially contributed to the adsorption of atrazine. This supports the findings of several workers mentioned above.

The nature of adsorption isotherms as illustrated in fig.3 also shows variations. The more attraction towards the adsorbents is evident by the shape of the adsorption isotherms for black soil of Dharwad. These isotherms are approaching a definite L-type which is characteristic of a situation where solid has high affinity towards the solute molecules. The isotherms for Ullal (S_1) and Kemmannagundi soils (S_2) have no definite L-shapes compared to those for black soils showing less affinity of solids towards the solute molecules.

The adsorbability values as indicated by Freundlich's 'K' values are high for soils having high clay content and organic matter. This confirms the findings of many workers (Harris and Warren, 1964; Talbert and Fletchall, 1965; Hamaker and Thomson, 1972). However, the addition of organic matter recorded higher 'K' values in all the three soils. Mithyantha (1973) and Rajanna (1983) reported that soil with organic matter showed higher values of 'K' for atrazine than in soils where organic matter was removed by chemical treatment. This confirms the importance of organic matter on atrazine adsorption.

The 'K' value for Kemmannagundi red soil recorded was 4.71 which increased to 8.39 when amended with organic matter. This perticular soil has lower native organic matter content.

Similar trend was observed for Ullal laterite soil also. In these two soils, increase in the capacity of atrazine adsorption in terms of Freundlich's constant is entirely due to the incorporation of organic matter. However, for the soil S_3, (Dharwad black) the major factor determining the adsorption in natural soil is clay content and the effect of organic matter is only secondary.

The adsorption studies in these soils brought out the importance of amount of clay, nature of clay and amount of organic matter on atrazine adsorption. Out of the three soils studied, Dharwad black soil reported maximum adsorption, mainly due to the contribution by clay content. In this soil, the influence of associated cations needs attention. The associated cations are also known to influence the extent of adsorption directly or indirectly (Jurinak, 1957; Morill et al., 1982). The cations not only alters the pH of the soil but also some polyvalent ions help to join coordinate bonds between clay surface and pesticide molecule (Greenland, 1965). In case of montmorillonite saturated with polyvalent cations like Ca^{++}, Cu^{++} etc. the protonation is belived to be due to highly polarised water molecule in direct coordination with cations. As such, in the present study, the Dharwad soil has recorded highest total exchangeable bases (30.5 me/100gm). The exchangeable cations like Ca^{++} and Mg^{++} together contributed to 28.5 me/100 gm, of which the contribution of Ca^{++} itself is 23 me/100gm. The Ca^{++} being a predominent cation its contribution on the adsorption capacity needs special emphasis. As observed in some South African soils, the complex formation as a possible mechanism of atrazine adsorption also needs to be investigated in these soils.

5.2 Persistence of atrazine in soils

Persistence of pesticides in soils has been defined by many workers as the time required to reduce the pesticide concentration to 75 to 100 per cent of the amount initially added (Hill and Mc Casty, 1967; Kearney et al., 1979). Later, a much broader definition of persistence has been given as the period during which a chemical remains intact and biologically active (Hiltbold, 1974).

Degradation of pesticides in soils is to a large extent mediated by microbes but considerable degradation does occur non biologically, like photo decomposition and chemical hydrolysis. Both biological and non biological degradation are more important and the processes operate simultaneously (Pionke and Chesters, 1973). The rate of degradation is largely dependent upon the soil type, adsorption-desorption equillibrium, moisture content, dose of application and nature of the compound.

In the present study, an attempt was made to findout the persistence and rate of degradation of atrazine in three soils of Karnataka viz. Ullal laterite (S_1), Kemmannagundi red (S_2) and Dharwad black (S_3) soils as affected by alternate wetting and drying of soils. This was done to simulate the irrigation schedule commonly practiced in the field. The rate of degradation was computed from the quantities of chemical remaining at different periods. The quantity not recovered is considered as decomposed since no attempt was made to identify the different path ways of degradation and the nature of degraded residues.

Two levels of atrazine namely 10 μg and 20 μg per 20 gm of soil were applied for all the three soils as given in chapter III. The actual quantities of chemical persisted at different periods are the result of overall effects of the factors influencing the degradation as mentioned above, in addition to the periodic addition of moisture to the soils. The results observed in different soils are discussed in the following paragraphs.

The differences in persistence of s-triazine in different soils are often reported by many workers. The results of persistence and degradation of atrazine as affected by wetting and drying cycles are discussed based upon the degradation kinetics. The data on persistence and degradation are given in the tables 6 to 11 and fig.3.

In the Ullal laterite soil (S_1), at the end of the first drying cycle, 85.5 per cent of added quantity remained in the soil irrespective of the level of application. When the soil was brought to field capacity on 11th day, the rapid degradation occured resulting in the lesser per cent recovery. The rate of degradation of atrazine in soils follows first order kinetics and the degradation rate constant 'K' for the Ist drying cycle (0 to 10 day) is 1.05 when expressed as K x 10^2/day(Table 15). When the soil was brought to field capacity on 11th day the K value suddenly increased to 6.7 showing a rapid degradation by wetting the soil. When the soil was allowed to dry, the rate constant came down to 1.11 (11 to 20th day). On the 21st day when the soil was again brought to field capacity the rate of degradation was faster recording 4.4 K value. However, the rate constant was reduced compared to the effect due to the wetting on 11th day. Again the degradation rate was reduced as the soils getting dried up. The trend was similar at both the levels of atrazine application.

For the soil S_2, the degradation per cent ranged from 4.5 to 47.0 at low level of atrazine application and from 4.0 to 47.5 at higher level of atrazine application over a period of 30 days. In otherwords, the per cent recovery ranged from 95.5 to 53, at low and from 96 to 52.5 at higher level of atrazine. The effect of wetting and drying on degradation of atrazine can be better understood by comparing the rate constant 'K' for first order reaction. In this soil also the trend was similar to that found in S_1 soil. The degradation rate constant ranged from 1.15 to 1.8 during Ist, IInd and IIIrd drying cycles and from 9.30 to 6.50 in the wet soils when the initial concentration was 10 µg. Similar trend was seen with higher concentration of atrazine too (Table 16). However, the effect of moisture on degradation rate in this soil was appreciably more than in S_1 soil.

Due to high adsorption of atrazine in Dharwad black soil, the per cent degradation recorded was lower than for the other two soils. The degradation rate constant as given in the table 17 clearly brings out the low rate of disappearence in this soil. The K values recorded ranged from 0.65 to 0.85 at low and from 0.6 to 1.05 at higher levels of atrazine during the dry periods. However, when the soil was watered, rapid degradation occurred recording the higher degradation rate constants. The values ranged from 9.9 to 3.1

Table 15. Degradation rate constant ($K \times 10^2$) and halflife ($t_{1/2}$) of atrazine in Ullal (S_1) soil as affected by wetting and drying processes.

Sl. No.	Periods	10 µg/20 gm soil		20 µg/20 gm soil	
		$K \times 10^2$/ days	$t_{1/2}$ days	$K \times 10^2$/ days	$t_{1/2}$ days
1.	First drying cycle (0 to 10th day)	1.05	66.00	1.20	57.75
2.	On 11th day (Soil at field capacity)	6.70	10.34	6.40	10.82
3.	Second drying cycle (11 to 20th day)	1.11	63.00	1.10	63.00
4.	On 21st day (Soil at field capacity)	4.40	15.75	4.70	14.74
5.	Third drying cycle (21st to 30th day)	1.30	53.30	1.20	57.75

Table 16. Degradation rate constant (K x 10^2/day) and halflife $t_{1/2}$ of atrazine in Kemmannagundi Red (S_2) soil as affected by wetting and drying processes.

Sl. No.	Periods	10 /ug/20gm soil		20 /ug/20gm soil	
		K x 10^2/ days	$t_{1/2}$ days	K x 10^2/ days	$t_{1/2}$ days
1.	First drying cycle (0 to 10th day)	1.15	60.26	1.20	57.75
2.	On 11th day (soil at field capacity)	9.30	7.45	11.90	5.82
3.	Second drying cycle (11 to 20 day)	1.40	49.50	1.30	53.30
4.	On 21st day (Soil at field capacity)	6.50	10.66	6.80	10.19
5.	Third drying cycle (21 to 30th day)	1.80	38.50	2.05	33.80

Table 17. Degradation rate constant (K x 10^2/day) and halflife of ($t\frac{1}{2}$) of atrazine in Dharwad black (S_3) soil as affected by wetting and drying processes.

Sl. No.	Periods	10 µg/20gm soil		20 µg/20gm soil	
		K x 10^2/ days	$t\frac{1}{2}$/ days	K x 10^2/ days	$t\frac{1}{2}$/ days
1.	First drying cycle (0 to 10th day)	0.65	106.61	0.60	115.50
2.	On 11th day (Soil at field capacity)	9.90	7.00	9.30	7.45
3.	Second drying cycle (10 to 20th day)	0.85	81.52	0.90	77.00
4.	On 21st day (Soil at field capacity)	3.10	22.35	4.00	17.32
5.	Third drying cycle (21 to 30th days)	0.85	81.52	1.05	66.00

10 μg atrazine and 9.3 to 4.0 with 20 μg atrazine when the soils were brought to field capacity. In this soil also addition of moisture increased the degradation process and effect of moisture was more pronounced than in S_1 soil.

The halflife periods of atrazine in different soils were computed from the degradation rate constant (K) values. The half life in S_1 soil ranged from 53.3 to 66.0 days when initial concentration of atrazine was 10 μg /20gm and from 57.75 to 63 days when the initial concentration of atrazine was raised to 20 μg/20gm during the dry period. When the soils were at field capacity $t_{1/2}$ ranged from 10.34 to 15.75 with low and 10.8 to 14.74 days with higher level of atrazine. Similar trend was observed in other two soils also (Tables 15, 16 and 17).

Natural factors are known to influence the rate of disappearence of pesticides through their effect on volatilization, downward movement, chemical and biological processess. Watering schedules are also found to effect the atrazine persistence and degradation in soils (Switzer and Rosem, 1960; Wilson and Cole, 1964). They reported that increase in moisture content decreased the persistence by increasing the degradation of atrazine in soils. In present study also, higher moisture decreased the per cent recovery in all the three soils.

Armstrong *et al*. (1967); Obien and Green (1969) conclusively proved that the mode of degradation of atrazine in soils was mainly by chemical hydrolysis. Atrazine is donverted to hydroxy atrazine resulting in considerable loss of its phytotoxicity. With the increase in moisture content of the soil, the rate of hydrolysis and subsequent conversion of atrazine to hydroxy atrazine also increased. In the present investigation when the soils were brought to field capacity degradation per cent increased, i.e. the degradation reaction was accelerated by the addition of moisture. Harris (1967) reported that chemical as well as biological degradation are favoured by moisture. According to him, in warm moist climate, the disappearence of triazines were more and longer persistence was observed in the dry periods. The results of present investigation confirms reports of many workers (Harris, 1967; Harris *et al*., 1969; Burnside, 1968; Hamilton and Arle, 1972; Skipper and Vok, 1972; Mithyantha, 1973; Koch, *et al*. , 1978) and this data help us to anticipate the fate of added organic weedicide under different water management practices.

In the present investigation, the persistence of atrazine is high in case of Dharwad black soil than in Ullal laterite and Kemmannagundi red soil. However, the rate and per cent degradation was more in S_2 (Red) soil than in S_1 (laterite) and S_3 (Dharwad) soils. More degradation in S_2 and S_1 soils may be due to more chemical hydrolysis because of low pH (Webber, 1970a). In S_3 soil, degradation was comparatively low obviously due to high adsorption of the chemical on the soil particles. However, moisture addition increased the degradation rate in case of S_3 soil, too. It is possible that as the soil water ratio decrease, the desorption may be acclerated and there by helping more degradation of even previously adsorbed molecules (Hilton and Yurn, 1966). This may be more relevant in the case of black soils.

In the present investigation, atrazine dissipation followed first order kinetics. The values obtained for persitence, the time required for the disappearence of atrazine lies within the range proposed by many research workers(Hilton and Yurn, 1966; Mithyantha, 1973; Swain, 1979; Pestemer et al., 1983).

5.3 Nutrient uptake by sorghum seedlings in the presence of atrazine

The wide spread use of herbicides for the control of weeds has made an important contribution to agriculture. A great deal of work have devoted on the behavior and transformation of herbicides in soils and the mechanisms by which they kill the weeds. The herbicides, besides having the target effect are also known to affect plants in several ways. Among them, nutrient uptake deserves more attention. Ion uptake capability of the roots is one of the parameter affecting the efficiency with which a plant recovers nutrients from the soil. Therefore, any agricultural practice interfering with the uptake process can influence fertilizer efficiency. Since the advent of weed control by means of chemicals, the question arose wheather this practice can affect the absorption capacity of nutrient by roots of economic plants.

A study was understaken to determine the effect of different doses of atrazine on the nutrient uptake by 17 days old jowar seedlings. The method employed was 'Neubauer technique' and the results of the findings are discussed in the following paragraphs.

5.3.1 Dry weight of seedlings

An increase in the dry weight of 17 day old sorghum seedlings with the application of atrazine was noticed. However, the increase was more when atrazine was applied at lowest concentration. But further increase in concentration decreased the dry weight. The increase in dry weight at low level of atrazine was 42.41 per cent over the control. This increase in dry weight may be due to its growth promotion action at lower concentration, which may result in better plant growth, shoot length, leaf blade and stem blade. A similar trend was observed by many workers (DeVries, 1963; Frency, 1965; Suseela Devi and Perur, 1978; Pawa and Jaiprakash, 1980; Channabasave gowda, 1986).

According to Kaufman and Kearney (1976) herbicide treated plots grow more vigorously and healthier than in plots where weeds are removed manually. This hormonal behaviour of herbicides especially of triazines were reported by earlier workers (Ashton and Crafts, 1973).

5.3.2 <u>Nutrient uptake by sorghum seedlings</u>

The effect of different levels of atrazine on the nutrient content and uptake by sorghum seedlings as given in table 13 and 14 revealed that, application of atrazine increased the N, P, K content had only little effect on Ca and Mg content. This increase in N, P and K content may be due to increase in nutrient uptake by the over all effect of herbicide on plant growth as indicated by the enhanced growth. Many workers conclusively proved that application of herbicide brought about metabolic changes in economic plants which results in decrease or increase in root growth and development. Some times these chemicals act as growth promoters which result in better plant growth, shoot length, leaf blade and stem diameter. This leads to better nutrient recovery from the soil. Also herbicides act on certain enzymes in economic plants (Suseela Devi and Perur, 1978; Ashton and Crafts, 1973) there by alter the normal physiology of the plant which ultimately have an effect on nutrient uptake. However, the herbicidal effect may be closely related to the age of the plant, its nutritional status and its sensitivity to the chemical (Wort, 1961). Recently Renosto,*et al*. (1970) reported that atrazine can affect the transport of nutrients in the roots through the plasma membrane.

In the present study also the increase in uptake of nutrients in presence of lower levels of atrazine are more pronounced. These findings confirms the work of many workers (DeVries, 1963; Frency, 1965; Eastin and Davis, 1967; Ries *et al*., 1967; Chopra *et al*., 1970; Hiran Pandi *et al*., 1972; Rotman *et al*., 1977 and Suseela Devi, 1978; Renosto *et al*., 1979; Pawa and Jaiprakash, 1980; R. Channabasave gowda, 1986).

Dhillon *et al*. (1966) reported that atrazine acts as growth promoting substance which resulted in better uptake of nutrient. Similarly Pawa and Jaiprakash (1980) reported the auxin type of action of atrazine and they concluded that this herbicide can act positively on the uptake of nutrients. Singh (1969) reported that s-triazines are known to increase the water absorption capacity of the plant. This also may contribute for increased nutrient uptake in the presence of atrazine.

The desire for quick and easy method of killing weeds gave rise to a large number of chemicals that are known as weedicides, but plants being a delicately balanced organism, any single change will have multiple effects. Though the target effects of these chemicals are known but their side effects on the economic plants especially on the nutrient uptake by plants in different soils need attention. The present study is only a modest attempt in this direction.

Whenever a schedule for chemical weed control is formulated, the chemical nature of the compound and the properties of the soil to which it is applied are to be taken into consideration. If the chemical is highly adsorbed on the soil, its bioavailability is going to be reduced. So also, presence of large quantity of organic matter. Again, the schedule of irrigation is likely to set a rythm of its degradation/disappearence thereby, affecting the bioavailability. Over and above, the crop plants will be subjected to many biochemical changes in the plant thereby altering the normal pattern of nutrient uptake. These are the main observations of this investigation.

SUMMARY

VI. SUMMARY

The present investigation was under taken in three parts. The first part includes the study on the extent of atrazine adsorption in soils and soils amended with recommended level of organic matter. Second part was on the persistence of this chemical in soils as affected by alternate wetting and drying of soils. The nutrient uptake by jowar seedlings as affected by application of atrazine at different levels formed the third part of this investigation. Soils used for the present study are Ullal soil (Ustocic distropept), Kemmannagundi soil (Oxic Rhodustalf) and Dharwad soil (Typic pellustat). They are denoted by the symbols S_1, S_2 and S_3 respectively. The important findings of the present investigation are as under.

1. A large portion of the added atrazine was adsorbed by the soils but the extent of adsorption was more when organic matter was incorporated. However, the amount of chemical adsorbed depended largely upon the nature of the soils.

2. In all the soils, the adsorption increased with the increase in concentration of atrazine, though the per cent adsorption decreased with increase in concentration. These trends were observed in all the soils studied.

3. The per cent adsorption of atrazine in S_1 ranged from 80 to 32.89 and 90 to 35.75 in natural soil and amended soil respectively, whereas in S_2, the per cent adsorption ranged from 75 to 34.32 and 90 to 35.75 in natural and amended soil respectively.

4. The per cent adsorption of atrazine in S_3 ranged from 90 to 37.75 and 100 to 42.9 in natural and amended soil respectively.

5. Among the three soils studied, S_3 adsorbed more amount of atrazine at all the levels than S_2 and S_1. Based on their capacity to adsorb atrazine, the three soils could be arranged in the order $S_3 > S_1 > S_2$. The same trend was observed in the organic matter incorporated soils also. However, addition of organic matter had more effect in S_2 on adsorption of atrazine. The differences in adsorption due to incorporation of organic matter was significant.

6. The values of Freundlich's constant 'K' were 5.79, 4.71 and 10.04 for natural soils S_1, S_2 and S_3 respectively. When the organic matter was incorporated, 'K' values also increased recording 8.67, 8.39 and 13.06 for soils, S_1, S_2 and S_3 respectively.

7. The highest 'K' value was obtained for S_3 and lowest for S_2 reflecting the properties of soil with respect to atrazine adsorption.

8. The values of 'n' recorded were 0.45, 0.39 and 0.59 in natural soils which increased to 0.56, 0.54 and 0.59 when organic matter was incorporated in S_1, S_2 and S_3 respectively.

9. Persistence of atrazine has shown a very close relation with moisture content of the soil. As the moisture content increased, the persistence decreased in all the soils.

10. Persistence of atrazine in terms of per cent recovery ranged from 95 to 59.5 in a span of 30 days under wetting and drying conditions in S_1 when the initial concentration of atrazine was 10 $\mu g/20$ gm soil. When the initial concentration of atrazine was increased to 20 $\mu g/20$ gm soil the persistence in terms of per cent recovery ranged from 95 to 57.5 for the same period.

11. In S_2 persistence of atrazine in terms of per cent recovery ranged from 95.5 to 53.0 at lower level of atrazine and 96 to 52.5 at higher level of atrazine, when the soil was incubated for 30 days with intermittent wetting and drying.

12. In case of S_3, persistence of atrazine in terms of per cent recovery ranged from 96 to 68 with 10 μg level of atrazine and 96 to 65 with 20 μg level when the soil was incubated for 30 days with intermittent wetting and drying.

13. Among the soils, persistence was more in S_3 than in S_2 and S_1. Based on the per cent recovery, the three soils could be arranged in the order of persistence as $S_3 > S_1 > S_2$. However the effect of moisture on persistence was more in S_3 than in S_1 and S_2 at both the levels.

14. The per cent degradation recorded in S_1 were 40.5 and 42.5 after 30 days of incubation with alternate wetting and drying when initial atrazine concentration was 10 and 20 μg/20g.

15. The per cent degradation in S_2 recorded were 47 and 47.5 when the initial concentration of atrazine was 10 and 20 μg/20 gm soil respectively after 30 days of incubation with alternate and wetting and drying.

16. In S_3 the per cent degradation was the lowest recording only 32 and 35 with 10 and 20 μg/20 gm soil respectively after 30 days of incubation with intermittent wetting to field capacity.

17. The order of degradation of atrazine with both the levels of atrazine addition was $S_2 > S_1 > S_3$.

18. The degradation rate constant ranged from 6.7 to 4.4 when the soil was at field capacity in case of S_1. When the soil was in the drying period, the rate constant recorded ranged from 1.05 to 1.30. The rate constants did not vary appreciably with initial concentration of atrazine.

19. In S_2, the degradation rate constants registered were 6.5 to 9.3 during the wetting period, and when the soil was in drying period the rate constants recorded were 1.15 to 1.80, when the initialy added atrazine level was 10 μg. When the initial concentration of atrazine was increased to 20 μg/20 gm, the rate constant recorded ranged from 11.90 to 6.8, when soil was at field capacity and from 1.20 to 2.05 when soil was in the drying period.

20. The degradation rate constant values ranged from 9.90 to 3.10 when S_3 was brought to field capacity. When the soil was in the drying period, the rate constant values recorded ranged from 0.65 to 0.85 when the initial concentration of atrazine was 10 μg. A further increase in the concentration of atrazine did not considerably alter the degradation rate constants.

21. The half lives calculated from degradation study revealed that when soils were at field capacity, the half life recorded was very low compared to the value recorded when there was limited moisture. The half life of atrazine in S_1 at field capacity was 10.34 to 15.75 days, in S_2 7.45 to 10.66 days and in S_3 7.0 to 22.35 days, when the added atrazine concentration was 10 μg/20 gm soil. During the drying period, the half lives in S_1 varied from 53.3 to 66.0 days, in S_2 38.5 to 60.26 days and in S_3 81.52 to 106.61 days. The initial concentration of atrazine had no considerable influence in the half life of the chemical.

22. The dry weight of 17 day old jowar seedlings increased to 3.66 g/pot with 0.25 kg a.i./ha of atrazine as against 2.57 g/pot in control amounting to an increase in dry weight by 42.51 per cent. With further increase in application rate of atrazine, decreased the stimulatory effect of atrazine, though the dry weight recorded was more than that of control seedlings.

23. The nutrient contents of jowar seedlings were also influenced by the application of atrazine. The per cent nitrogen content was significantly more at all the levels of atrazine though the maximum N content was recorded with the lowest level of atrazine. In case of P, though

numerical increase in P content was noticed in all the levels of atrazine, significant increase in P content was noticed only in the treatment with atrazine @ 0.25 kg a.i./ha. Similar results were observed in case of K also. The Ca did not record any general trend while Mg content was significantly reduced by herbicide application.

24. The nitrogen uptake increased significantly with the application of atrazine at all the levels. The maximum N uptake was observed in the presence of atrazine at the lowest concentration i.e. 0.25 kg a.i./ha. A similar trend was observed for P and Mg uptake also. As far as K and Ca uptake were concerned the maximum uptake was recorded with atrazine at the rate of 0.5 kg a.i./ha.

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* Original not seen.

APPENDICES

Appendix-I

Pooled data of Ullal (S_1) soil

Textural class	- Loamy sand (Ustoxic Distropepts)	
Electrical conductivity mmhos/cms	- 0.078	
Organic carbon (%)	- 0.83	
Cation exchange capacity (me/100g)	- 17.80	
Total exchangeable bases (me/100g)	- 5.10	
Percent base saturation	- 28.65	
Maximum water holding capacity(%)	- 23.20	
Dominent clay mineral	- Kaolinite	
Amount of clay (%)	- 10	
Adsorption parameter	**Natural soil**	**Amended soil**
K - value	5.79	8.67
n - value	0.45	0.56
Degradation rate constant	**10 µg level**	**20 µg level**
Average rate constant for dry period	1.15	1.16
Average rate constant for wet period	5.52	5.52
Halflife values (days)		
Average $t_{1/2}$ for dry period	60.73	59.48
Average $t_{1/2}$ for wet period	13.05	12.78
Quantity of atrazine degraded 30 days after application (%)	40.50	42.50

Appendix - II

Pooled data of Kemmannagundi (S_2) soil

Textural class	-	Sandy clay (Oxic Rhodustalf)
Electrical conductity mmhos/cms	-	1.55
Organic carbon (%)	-	0.61
Cation exchange capacity (me/100g)	-	20.10
Total exchangeable bases (me/100g)	-	8.50
Percent base saturation	-	42.29
Maximum water holding capacity(%)	-	39.48
Dominent clay mineral	-	Amorphous type
Amount of clay (%)	-	22.00

Adsorption parameter	Natural soil	Amended soil
K - value	4.71	8.39
n - value	0.39	0.59

Degradation rate constant	10 µg level	20 µg level
Average rate constant for dry period	1.45	1.52
Average rate constant for wet period	7.90	9.35
Halflife values (days)		
Average $t_{\frac{1}{2}}$ for dry period	46.48	41.62
Average $t_{\frac{1}{2}}$ for wet period	9.01	8.01
Quantity of atrazine degraded 30 days after application (%)	48.00	47.50

Appendix - III

St Pooled data of Dharwad (S_3) soil

Textural class	- Clay loam (Typic Pellustat)	
Electrical conductivity mmhos/cms	- 1.725	
Organic carbon (%)	- 0.54	
Cation exchange capacity (me/100g)	- 52.50	
Total exchangeable bases (me/100g)	- 30.50	
Percent base saturation	- 58.10	
Maximum water holding capacity(%)	- 52.21	
Dominent clay mineral	- Montmorillonite	
Amount of clay (%)	- 46.00	
Adsorption parameter	Natural soil	Amended soil
K - value	10.04	13.06
n - value	0.55	0.59
Degradation rate constant	10 µg level	20 µg level
Average rate constant for dry period	0.78	0.85
Average rate constant for wet period	7.50	7.50
Halflife values (days)		
Average $t_{1/2}$ for dry period	89.88	86.16
Average $t_{1/2}$ for wet period	14.68	12.38
Quantity of atrazine degraded 30 days after application (%)	32.00	35.00