University of Nevada
Reno

Enhancement of Photodegradation of Pesticides by Transport Upward in Evaporating Water

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in Hydrology/Hydrogeology

by

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August 1994

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Abstract

Photolysis of pesticides is limited to the surface 0.5 mm in soils due to light attenuation by naturally occurring chromophores. Processes which transport chemicals into this light-irradiated zone can enhance rates of photolysis. Three water-soluble pesticides with differing aqueous photolysis half-lives, sorption coefficients ($K_d$) and volatility were chosen to determine the effectiveness of transport and evapoconcentration in enhancing photolysis rates. Napropamide, imazaquin and pentachlorophenol (PCP) were incorporated into loamy sand ("Callahan") or sandy clay loam ("Montana") soils. Soils subjected to differing flow regimes were irradiated with ultraviolet light or sunlight for varying time periods. Photolysis was most rapid in Callahan soil containing napropamide, with 70% lost after 14 days of sunlight irradiation for both near-saturated and unsaturated flow treatments. Loss of napropamide was much slower in Montana soil, with 29% lost after 14 days. Transport to the soil surface was retarded in this soil, reflecting a $K_d$ of 6.6 to 7.2 mL/g vs. 0.4 to 0.72 mL/g in Callahan soil. Photolysis of imazaquin was somewhat slower, with 55% lost in Callahan soil after 14 days of sunlight irradiation, and 29 to 31% in Montana soil after 14 days. Little sorption was measured for imazaquin in either soil, allowing rapid upward transport but also increased depths of downward diffusion, decreasing the extent of photolysis. PCP, which is moderately volatile, was initially photodegraded rapidly in Callahan soil undergoing near-saturated flow,
with up to 55% lost in sunlight-irradiated treatments. Rates of transport of PCP were slower in Montana soil, reflecting a measured $K_d$ of 10 mL/g vs. 0.4 mL/g in Callahan soil. Despite this, similar amounts of photolysis of PCP had occurred after 14 days in both soils. As the soil profile became increasingly dry due to surface evaporation, more was lost via volatilization than photolysis in both soils, with up to 77% lost from dark controls in 14 days. In soils subjected to periodic infiltration events, downward redistribution of napropamide and imazaquin occurred, with the most photolysis measured when there was no sorption, as when imazaquin was applied to Callahan soil, or when sorption retained chemicals at the soil surface.

IUPAC Nomenclature:

napropamide: 2-(α-naphthoxy)-N,N-diethylpropionamide

imazaquin: 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolinecarboxylic acid
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Chapter 1:
The Effects of Sorption and Transport on the Photolysis of Organic Compounds on Surfaces
I. Introduction

Photolysis is the process in which absorption of light results in a transformation of chemicals. These transformations can significantly alter the toxicity and physical characteristics of the compound, resulting in products which may be more or less readily degraded or transported in the environment. Chemicals can undergo direct photolysis, in which light is absorbed by the compound, resulting in an excited state, or indirect (sensitized) photolysis, in which the compound of interest reacts with another chemical (or sensitizer) which has absorbed light and is in the excited state. The efficiency of these processes is dependent upon the medium in which the molecule exists (Choudhry and Webster, 1985).

Phototransformations of medium weight organics may occur in air, water or on soil, plant or other surfaces. The medium of water has been the most thoroughly studied (Miller & Zepp, 1983; Miller & Crosby, 1983; Marcheterre et al., 1988), with less known about photolysis on surfaces and in air. Increasing attention is focusing on photolysis of organic compounds as a mechanism for the decontamination of soil, especially in relation to other degradation mechanisms. Solid surfaces are highly variable, heterogeneous systems which are difficult to categorize and study; yet these same surfaces often are the recipients of many pollutants from a variety of sources (Miller et al., 1989).
In this paper, we will review the current state of knowledge concerning photodegradation of organic chemicals on solid surfaces, with an emphasis on those properties of soils which govern the rate and efficiency with which phototransformations may occur.

II. Basic Principles of Photochemistry

a) Direct photolysis

The first law of photochemistry, the Grotthus-Draper Law, states that "only light which is absorbed by a molecule can be effective in producing a photochemical change in the molecule" (Calvert and Pitts, 1966). In direct photolysis, the light absorbed by the parent compound, \( P \), results in an excited state:

\[
P \xrightarrow{k \nu} P^*\]

If the minimum amount of energy applied to the system is at least as energetic as the bonds to be broken, then a transformation may occur. Since most bond dissociation energies are greater than 30 kCal/mole, only energy from the ultraviolet/visible portion of the spectrum from 110 to 750 nm will be effective in breaking bonds (Calvert and Pitts, 1966). As incoming sunlight with a wavelength less than 290 nm is absorbed by the ozone layer in the earth's stratosphere, this range is effectively truncated at 290 nm. Sunlight is also
attenuated via absorption by atmospheric gases and through molecular and particle scattering.

The absorption of light can be expressed as a function of wavelength by the Beer-Lambert Law (Finlayson-Pitts and Pitts, 1986):

\[
\frac{I(\lambda)}{I_0(\lambda)} = 10^{-\varepsilon C l}
\]

where \(I_0(\lambda)\) is the intensity of light of wavelength \(\lambda\) incident on the front of a column of a single absorbing species; \(I(\lambda)\) is the intensity of light transmitted through the column of material; \(C\) is the concentration of the absorbing species in moles L\(^{-1}\); \(l\) is the pathlength of the absorbing column in cm; \(\varepsilon\) is the molar extinction coefficient in L mole\(^{-1}\) cm\(^{-1}\) (also referred to as molar absorptivity); and \((I/I_0)\) is the absorbance \(A\), or molar absorbance. The absorbance can be measured directly using UV absorption spectrophotometers and \(I(\lambda)\) can be calculated using a chemical actinometer (Calvert and Pitts, 1968; Miller and Zepp, 1983).

The rate of direct photolysis is proportional to the rate of absorption of light by the compound when it is at a low concentration in the environment, and the efficiency with which the absorbed energy results in the formation of products, or the reaction quantum yield. In general, photochemical reactions are relatively inefficient, with most excited molecules returning to the ground state rather than resulting in transformations. Quantum yields of organic
compounds in aqueous systems are often less than 0.01. Deactivation of the excited molecule can occur by luminescence, or emission of electromagnetic radiation; physical quenching, in which the excited species loses energy to another atom or molecule, with the energy being dissipated as vibrational energy, or heat; electron transfer; and photoionization; as well as phototransformation (Calvert and Pitts, 1966; Finlayson-Pitts and Pitts, 1986; Schwartzenbach et al., 1993).

The reaction quantum yield, $\phi$, of a compound is defined as (Choudhry and Webster, 1985):

$$\phi_{r,\lambda} = \frac{\text{number of molecules decomposed}}{\text{number of quanta absorbed}}$$

First-order kinetics will then generally apply for dilute solutions at the given wavelength, allowing calculation of the rate constant ($k_{p,\lambda}$) in sec$^{-1}$ for the photolysis of organic chemicals, such that

$$\ln\left(\frac{C_0}{C_t}\right) = k_{p,\lambda} t$$

where $t$ = time in seconds, and $C_0$ and $C_t$ are the concentrations of the compound (mol L$^{-1}$) at times zero and $t$. The slope of a plot of $\ln (C_0/C_t)$ vs $t$ yields a value of the photolysis rate constant, $k_{p,\lambda}$ which can then be used to calculate the reaction quantum yield $\phi_{r,\lambda}$ as follows:

$$\phi_{r,\lambda} = \frac{k_{p,\lambda}}{2.3031 \varepsilon \lambda}$$
where \( I_\lambda \) is the intensity of light of wavelength \( \lambda \); and the half-life for photodegradation (assuming first-order kinetics) as

\[
(t_{1/2}) = \frac{\ln 2}{k_p} = \frac{0.693}{k_p}
\]

Estimating sunlight photolysis rate constants of pollutants requires summing the sunlight absorption rate over all the wavelengths of sunlight that are absorbed by the compound. Values for solar intensity data as a function of time of day, season, and latitude for the range \( \lambda = 297.5 \) to 800 nm are given in Zepp and Cline (1977), or can be calculated using models such as GCSOLAR (U.S. EPA, 1988).

Predictions of the potential for direct photolysis can be made first on the basis of the presence of chromophores, or functional groups which absorb light. Chromophores include functional groups containing an unsaturated heteroatom (C=O, C=C, N=N, NO\(_2\)), as well as extended hydrocarbon systems such as phenanthrene (Calvert and Pitts, 1966). Likewise, an assessment of the potential for direct absorption of light can be made by determining the spectral overlap between the absorbance spectrum of the compound and the emission spectrum of the light source with which it is being irradiated (Liefer, 1988). It must be noted, however, that the absorbance spectrum will vary depending upon the solvent used and the physical state of the compound.
b) Indirect photolysis

Indirect or sensitized photolysis is a process in which a sensitizer absorbs light to form an excited state sensitizer $S$:

$$S \rightarrow h\nu \rightarrow S^*$$

which may be in either the singlet ($^1S$) or triplet ($^3S$) state. The excited state sensitizer can lose energy and return to the ground state:

$$S^* \rightarrow S$$

or can result in an energy transfer to the compound $P$ of interest:

$$S^* + P \rightarrow S + P^*$$

The excited compound may then degrade to yield various products. The sensitizer can also produce reactive substances which may react with the pollutant, such as singlet oxygen, or radicals and oxidants (Miller and Crosby, 1983). Reactions with oxidants are thought to be more important than those involving triplet state energy transfer to $P$. Singlet oxygen, in particular, is important for reactions with electron-rich compounds (Foote, 1976). If the energy from the sensitizer is transferred to another compound, the energy can instead be lost in a process called quenching, and is no longer available to produce phototransformations.

Sensitizers include naturally occurring organic and inorganic species, among which humic substances, clay minerals and transition metals are associated with surfaces, as well as in aqueous systems (Wolfe et al., 1990;
The effect of the photosensitizer depends upon the wavelength of irradiation, the reaction media, and the UV absorption of the substrate and the photosensitizer (Tsao and Eto, 1994). Recognition of sensitizers in the environment is crucial to understanding indirect photochemical transformations, which cannot be readily predicted as are those of direct photolysis.

**c) Photochemical Reactions**

Photochemical reactions in organic molecules include fragmentation, intramolecular rearrangement, isomerization, hydrogen atom abstraction, dimerization, and electron transfer from or to the chemical. These reactions, which include those commonly seen in other transformation reactions, as well as some which are unique to photochemistry, have been summarized in Harris (1982). Of these reactions, photooxidation is probably the most important, given the presence of oxygen in most environmental compartments (Miller and Crosby, 1983). Oxygen reacts rapidly with free radicals, and can produce many oxidants. Oxidations include ring and aromatic side chain oxidations, N-oxidations, S oxidations, and phosphorothioate to phosphate oxidations. These reactions can occur as both direct and indirect processes, and can yield daughter compounds of both greater and lesser toxicity.

Photohydrolysis reactions can also result in compounds of lower toxicity than the parent compound via production of phenols, or photonucleophilic
substitution. Photoreductions produce halogen replacement by hydrogen and reduction of aryl nitro groups. The degree to which photoreduction will be a significant pathway depends upon the availability of hydrogen sources. The matrix in which the sample occurs will thus influence the degree to which photoreduction will be significant, and the presence or absence of oxygen will alter the photoproduct composition (Miller and Crosby, 1983).

Products of photochemical reactions often have increased polarity and reduced solvent extractibility, resulting in an increase in bound residues in the presence of sediment or other solids (Harvey et al., 1985; Miller et al., 1988). This increase in polarity may enhance the ability of microorganisms to further degrade the substance. Pignatello et al. (1983) found that sunlight irradiation of pentachlorophenol in river water initially resulted in more polar photoproducts which were more readily biodegraded. Photodegradation also reduced the toxicity of the compound to levels at which microorganisms were able to survive.

Many other photochemical transformations may occur, with the reaction type dependent on the structure of the parent compound. A review of phototransformation of herbicides was presented by Marcheterre et al. (1988). It must be emphasized that the majority of molecules which absorb light will return to the ground state by a variety of physical processes, and thus will not be structurally altered.
d) Factors affecting rates of phototransformations

The rate equations and expressions for photolysis which have been presented were developed for model systems in which organic compounds are present at low concentrations in aqueous systems. Light transmission through water can be attenuated in the presence of particles in the water, both by light absorption and light scattering. In general, a decrease in direct photolysis rates of dissolved pollutants occurs as particle concentrations increase, suggesting that light absorption is the more significant effect (Miller and Zepp, 1979a). In some cases, however, the effect of light scattering results in enhanced photolysis rates in clay suspensions.

Likewise, sunlight intensity will vary with the time of day and year, with a maximum occurring during mid-day in the summer months. An attempt was made to normalize natural sunlight exposure to that of an artificial xenon light source by assuming that total daily radiation was approximately equivalent to 0.75 times 12 hours of midday radiation (Parker and Leahey, 1988). The ratio $A$ of light intensity under the xenon lamp to that of mid-day sunlight at a given latitude and season was calculated from measurements of the intensity of both light sources. Assuming a 12 hour day, $12/A$ is equivalent to 12 hours of midday sunlight, and $(12/A)*0.75$ is equivalent to one day of sunlight at that latitude and season. This method is limited by its assumptions and fails to account for variations in cloud cover, pollutants, or other weather conditions over the daily
Another approach is to sum radiation intensity over the course of a day and compare it to that measured under artificial lights.

If the compound is present in high concentrations, the compound itself may affect light penetration through the entire depth of the solution (Miller and Zepp, 1983). Photochemical reactions may also be somewhat temperature dependent. It has been estimated that a 10 °C increase in temperature might accelerate a reaction by a factor of 1.15 to 1.5 (Schwarzenbach et al., 1993). The dependence will occur when the reactions require a second reactant, resulting in temperature-dependent kinetics.

Rates of reactions will also vary with the composition of the system. In the presence of solid particles, sorption of pollutants to these particles may result in lower rates of transformation due to light shielding. The absorbance spectrum of the sorbed chemical may also be significantly changed as compared to that of the dissolved compound (Parlar, 1992). Since the molecular environment is changed, sorbed species may have different quantum yields and product distributions (Katagi, 1991; Miller and Zepp, 1979b). Indirect processes involving surfaces may also be altered, both in terms of rates and photoproducts.

III. Properties of Surfaces Which Alter Photochemical Reactions

The presence of solid surfaces can greatly alter photochemistry from that encountered in aqueous solutions. Kinetics of photoreactions involving soil or
plant surfaces do not follow the first order equations previously presented, and efforts to quantify these processes have not yet been successful. The majority of research has centered on photolysis of pesticides in soils, given their widespread use and potential for environmental contamination, but the heterogeneity of the system makes quantification difficult. The following discussion is presented in an effort to define the properties of mineral surfaces, primarily soils, which may have an effect on photodegradation of xenobiotics.

Soil consists of three phases: a solid phase consisting of both organic and inorganic solids, which are often associated in organic matter-clay complexes (Saltzman and Mingelgrin, 1984); a liquid phase; and a gas phase. The liquid and gas phases are important to the transport of soluble and volatile chemicals in the soil, whereas the solid phase is the primary site for chemical accumulation and transformations. The range of sizes of particles in soils is referred to as soil textural fractions, which encompass gravel (>2 mm in diameter), sand (from 0.05 - 2 mm), silt (.002 - .05 mm) and clay (<0.002 mm) according to U.S. Department of Agriculture classifications. While it is generally accepted that most organic chemical sorption in soils is related largely to the organic matter content, organic surfaces have been shown to be much less active than mineral ones in inducing chemical degradation of pesticides. At soil surfaces, where organic contaminants are subjected to sunlight irradiation, the
relative contribution of soil organic matter in retarding movement and photolysis may be more important than its activity in inducing reactions.

a) Soil mineral fraction

The soil mineral fraction consists of inorganic components including those which have a definite crystalline structure, as well as amorphous non-crystalline oxides. Primary minerals are those formed at elevated temperature and pressure and are essentially unchanged from igneous or metamorphic rocks. The most common primary minerals in soils are quartz and the feldspars (Bohn et al., 1985). These primary minerals form the bulk of the sand and silt size fractions. Minerals of the finest size fraction are formed by low temperature reactions and either inherited from sedimentary rocks or formed by weathering. Secondary minerals in soils include carbonate and sulfur minerals, the layer silicates, and various oxides. The most important of these are probably the layer silicates, found in the clay fraction of soil, and the free oxide minerals, which form as soils are depleted of silicon by leaching. Hydrous oxides and amorphous aluminosilicates are the most important non-layer minerals, and are often found attached to or coating other mineral particles.

The sand and silt size fractions of the soil provide the physical structure, and the smaller size clay and amorphous oxides provide the chemical character of the soil due to their large surface area to volume ratio and the overall charge on the particle.
Soil clays are generally less well ordered and smaller in size than the pure minerals they include (Bohn et al., 1985). The particles may be coated with iron and aluminum oxides or organic matter to further complicate their behavior. These coatings influence mineral properties such as cation exchange capacity (CEC) and surface area values, and may restrict the swelling and collapsing of expansible minerals, while oxide coatings increase the properties associated with positively charged surfaces, resulting in the retention of anionic species in soils (Buchter et al., 1989).

Clays have been shown to accelerate degradation of organic substances when indirect processes are active (Katagi, 1990; Katagi, 1991). Irradiation of clays, especially kaolinite, resulted in the formation of hydrogen peroxide, which acted as a sensitizer in the photodegradation of tolclofos-methyl on clay films in a temperature controlled experiment purged with water vapor saturated air and irradiated with a xenon arc lamp (Katagi, 1990). The primary photoproduct resulted from the oxidation of the P=S bond. Photoinduced formation of singlet oxygen on the clay surface was not detected. Katagi (1991) also investigated the photodegradation of esfenvalerate on kaolinite, montmorillonite, humic acids and sandy clay loam soil in a similarly controlled experiment. The greatest increase in rates of degradation occurred on kaolinite, with little difference seen on the soil. Katagi speculated that Ti, Fe, Zn or Mn metal oxides may act as photocatalysts on clay surfaces.
Clays are also used to photostabilize pesticides to retard their sunlight degradation. Rozen and Margulies (1991) found that adsorption to montmorillonite, nontronite and hectorite resulted in significant photostabilization of tetrahydro-2-(nitromethylene)-2H-1,3-thiazine (NMH). Co-adsorption of a cationic dye improved stabilization. Deactivation was speculated to occur via energy transfer between the two organic molecules adsorbed on the surface of the clay. In a later experiment, Margulies et al. (1992) demonstrated considerable photostabilization of trifluralin adsorbed on montmorillonite clay, both with and without the organic cation thioflavin T. Based on Fourier-transform infrared spectroscopy of the complex, the authors suggest that photostabilization is due to steric hindrance imposed by the clay surface to the cyclization step of the photochemical reaction.

Metal oxide particles in soils may also act as photochemical catalysts for both oxidative and reductive transformations (Miller et al., 1987). Manganese, iron and titanium oxides can be relatively abundant, with titanium dioxide (TiO₂) showing marked stability in soils during weathering. Mansour et al. (1989) demonstrated the role of TiO₂ in the photodegradation and oxidative cleavage of carbetamide and carbofuran. The metal oxide was more effective than was the presence of humic acid or soil suspension.
b) Soil organic fraction

The organic fraction of soil includes living organisms and recognizable dead plant and animal residues and humus. This portion of the soil environment is in constant flux as a result of changing environmental conditions, land use, and microbial transformations. Decay of soil organic matter (SOM) to form humus will proceed as long as oxygen, water, temperature, pH and nutrient levels are sufficient for the decomposing organisms. After rapid initial breakdown of plant residues, resistant fractions may develop which have lifetimes of 250 or more years (Stevenson, 1982).

Humus is a mixture of brown to nearly black amorphous and colloidal substances with high specific surface area (Bohn et al., 1985). This substance consists of organic matter which has been transformed by soil microorganisms into a relatively stable form in which the morphological characteristics of the parent compound are no longer evident. Humic acid molecules are polymers which contain a high density of reactive functional groups. These molecules vary in structure and density of functional groups while having about the same basic structure. They are characterized by their ability to be precipitated at pH 1 on acidification of aqueous alkaline extracts (Hayes, 1984). Fulvic acids are low molecular weight compounds which have higher oxygen contents and lower carbon contents than do humic acids, making them more water soluble as well.
as soluble in both aqueous acids and bases. Humins are the residues which are insoluble in these solvents.

In combination with clay minerals, humus influences soil stabilization via the formation of aggregates, increasing permeability as well as aeration. Humus also has a very high water holding capacity, potentially absorbing 80-90% water by weight (Bohn et al., 1985). Low molecular weight components of organic matter, such as fulvic acids, will form stable complexes with various metal ions or other polyvalent cations. Organic matter content is also closely correlated with organic chemical sorption in soils.

Dissolved organic matter (DOM) in natural waters has been shown to photosensitize the degradation of various organic pollutants (Mabury and Crosby, 1994). Photolysis of DOM can result in the generation of hydroxyl radicals via homolytic cleavage of humic acid (Takahashi et al., 1988). Hydroxyl radicals are extremely reactive towards many organic compounds. Humic substances can also transfer electronic energy directly to the pollutant, causing chemical transformations.

Despite evidence that irradiation of organic matter may be involved in chemical degradation, Smith et al. (1978) found no correlation between photolysis rates of methidathion and organic matter content in an experiment using six dry soils varying in organic matter content from 0.1 to 20%. Haag et al. (1991) found neither increases nor decreases in rates of photolysis of diethylene
glycol dinitrate in humic solution, despite speculation that reactions might occur
with photo-produced free electrons from humics. Katagi (1991) found
accelerated rates of photolysis of esfenvalerate on humic acids, which were due
to indirect processes involving the photogeneration of hydrogen peroxide or
hydroxyl radical. Minero et al. (1992) found that dissolved humic substances
from a soil extract resulted in more rapid photodegradation of atrazine,
presumably due to surface-assisted processes of degradation, including
production of singlet oxygen, hydroxyl or peroxy radicals, and hydrogen
peroxide. They concluded that adding humic acids at 10 ppm of organic carbon
would increase the photolytic degradation of atrazine by a factor of three in the
presence of simulated sunlight.

c) Charge distribution on surfaces

The chemical properties of soil mineral particles, primarily clay minerals,
and the soil solution have a profound effect on the properties of soils. Many of
these properties can be understood by examining the development and structure
of clay minerals, and the resultant overall charge which may then extend over
the particle surface. The subject is covered in greater depth in standard soil
chemistry texts (Bohn et al., 1985; Bolt and Bruggenwert, 1976).

Layered silicates (e.g. clay minerals) can be differentiated by structure
(the number and sequence of tetrahedral and octahedral sheets), the layer
charge per unit cell structure, the type of interlayer bonds and cations present,
the cations found in the octahedral sheet, and the type of stacking. During development of minerals, it is common for an overall net negative charge on the particle to develop as a result of isomorphous substitutions in both the tetrahedral and octahedral layers of the crystalline structure. Replacing Si$^{4+}$ by Al$^{3+}$ in the tetrahedral sheets yields a net negative charge, as does the replacement of Al$^{3+}$ by Mg$^{2+}$ in the octahedral layers. Another source of unbalanced charge in clay crystals results from incomplete charge neutralization of terminal atoms on lattice edges, on broken particle edges, or in amorphous constituents.

Charge development can be divided into two basic categories: pH independent charge, which arises from the permanent negative charge in the inorganic fraction; and pH dependent charge, which varies with the pH of the soil solution and can occur both with clay particles and with soil organic matter such as humus. As pH decreases, protonation may occur on functional groups on the edges of clay particles, resulting in the generation of a positive charge. The overall consequence of charge development in clay particles is the external adsorption of compensating ions, mostly concentrated near the exterior surface of the particle, in an effort to reach electroneutrality. This gives rise to both the cation exchange capacity of the soil and to mechanisms of anion adsorption, including specific and non-specific adsorption, and molecular retention.
In dry soils, these compensating ions are found in close association with the mineral surfaces. As soil moisture increases and wetting of particles occurs, the adsorbed ions become distributed throughout the liquid layer surrounding the clay particle, which acts as a multiple anion. The concentration of adsorbed cations is greatest closest to the particle surfaces, and decreases exponentially with distance from the surface. This is a result of the opposing tendencies of attraction to the negatively charged surface, and outward diffusion of ions in an effort to equalize solution concentrations, maximizing entropy. The composition of ions in this layer surrounding particles is thus different from that of the bulk solution.

The configuration of charged particle surrounded by ions in solution has been called the electrostatic or diffuse double layer (DDL). The extent of this layer is governed by the concentration of ions in the bulk solution (increasing the concentration reduces the double layer) and by the valency of the ions in solution. Doubling the valence (i.e. from Na\(^+\) to Ca\(^{2+}\)) will halve the extent of the double layer.

The concept of cation exchange arises from the electrostatic double layer. Cations or anions within the DDL can be replaced by other ions entering with the soil solution. Ion exchange varies with pH, due to pH dependent charge generation. The dominant type of exchange is cationic due to net negative permanent charge development in clay minerals. Cation exchange capacity
(CEC) depends on the specific surface and charge density of the individual particles, and will be highest for soils which are high in clay and organic matter (Bohn, 1985; Pignatello, 1989). CEC is important in the movement and retention of ions.

d) Sorption of organic compounds to surfaces

Sorption of organic compounds retards their movement through the soil, with the extent of retardation dependent upon the physical and chemical properties of the soil, as well as the molecular characteristics of the pesticide (Wagenet and Rao, 1990). Adsorption is a more specific term which refers to a process involving the attraction and retention of a chemical on the surface for a time that depends on the affinity of the chemical for the surface. Retention mechanisms involved in sorption of organic compounds to soils include London-van der Waals forces, hydrogen bonds, cation and water bridging, anion exchange, ligand exchange, protonation of the organic functional group, cation exchange, covalent bonding, and physical trapping in the soil matrix (Koskinen and Harper, 1990).

Charge development on soil surfaces is thus one means by which sorption may occur. Organic compounds which are ionizable, such as weakly basic or acidic compounds, can adsorb by ionic mechanisms at certain soil pH's. Sorption of nonionic organic compounds is dominated by the organic fraction of the soil when the total organic carbon content of the soil is greater than 0.1%
Retention of these compounds may occur via a partitioning of the chemical between the aqueous phase and the hydrophobic organic matter (Chiou et al., 1979), although this may be an oversimplification.

Sorption of organic compounds is affected by a number of factors, including temperature. Since adsorption is usually an exothermic process, as temperature increases, adsorption is expected to decrease. However, higher temperatures can increase rate processes, which tends to negate the decrease in adsorption (Hamaker and Thompson, 1982). Murray and Hall (1989) found significant differences in adsorption of 3,6-dichlorosalicylic acid in certain soils at 15, 25 and 35 °C, with adsorption decreasing at increasing temperatures, suggesting an exothermic bonding process. Zhang et al. (1990) determined that neutral organic molecules are adsorbed in an endothermic fashion, being distributed between the interfacial phase and the bulk phase.

Changes in soil water content will change the fraction of the chemical which is adsorbed. As the soil dries out, the fraction of the chemical adsorbed will increase. Cation exchange capacity and soil pH will also influence sorption. As pH decreases, the concentration of hydrogen ions becomes competitive with cations, decreasing sorption. The soil itself will change with the pH, and protonation of molecules may result in greater clay sorption. Salts can be active in displacing cations from the soil ion exchange matrix, or may change the
activity of the adsorbate in solution, changing the charge density associated with the soil adsorptive surface.

Measurement of estimates of sorption on soils or sediments can be made using a simple laboratory technique, in which soil samples are equilibrated with aqueous solutions of the compound of interest at known initial concentrations (Rao and Davidson, 1979). Changes in solution concentrations following a period of shaking and equilibration are attributed to sorption of the compound onto the soil. Many variables must be considered, including soil/solution ratio, temperature, condition of the soil, the type of vessel used, and the type of agitation chosen (Green and Karickoff, 1990).

In general, for organic compounds at low concentrations in the soil, data from batch equilibrium studies can be plotted as linear adsorption isotherms such that

$$c_s = K_d c_L$$

where \(c_s\) is sorbed phase concentration, \(c_L\) is solution phase concentration, and \(K_d\) is the sorption coefficient. The precision of this method decreases as sorption decreases.

Because adsorption is positively correlated to the organic carbon content of the soil, sorption coefficients are often expressed as the organic carbon sorption coefficient \(K_{oc}\), by dividing \(K_d\) by the organic carbon content. Methods

Batch equilibrium experiments are complicated by transformations which may occur during the equilibration period. The use of initially air dry soil, a brief equilibration period and low temperature can minimize these effects (Dao et al., 1982); however, these are all factors which can themselves alter sorption results. Other models which are commonly used to describe adsorption data include the Langmuir, Freundlich and Brunauer-Emmett-Teller (BET) equations. A discussion of these methods can be found in Bailey and White (1970) or Bohn (1985).

The assumption of describing sorption as a linear, equilibrium, reversible process is not always valid. Hysteresis in adsorption/desorption studies is often seen as a consequence of binding mechanisms which are not reversible, such as specific ion adsorption. Degradation may account for some of the observed hysteresis, or changes in the composition of soil surfaces or slurry during the course of batch equilibrium experiments may cause apparent hysteresis. Centrifugation of the samples prior to measuring soil concentrations may affect desorption, or incomplete centrifugation may lead to the removal of some suspended sediment on each analysis. (Koskinen and Harper, 1990).

Alternately, some compounds may be so strongly bound to soil surfaces that little or no desorption occurs, especially at low rates of application (Cheng et
In these cases, the compound may either react irreversibly with the soil surface, or desorption equilibrium, being a slower process, may take prolonged intervals to achieve. Pignatello (1989) suggests that entrapment of chemicals in soil "micropores" may be responsible for retarding degradation or transport. This theory has been expressed as a two site model for sorption, in which xenobiotics may be sorbed to the surface of the particle in a labile fraction, or as a less labile fraction within the particle interior (Karickhoff and Morris, 1985). These models divide possible sorption domains into two kinetic fractions: one on which sorption is assumed to be instantaneous, and one on which the process is assumed to be time dependent as a function of sorbent constituents (Wagenet and Rao, 1990). Alternatively, two-region models assume sorption is at equilibrium, with transfer to some sites being diffusion controlled (Gamerdinger et al., 1990). Criteria for the validity of local sorption equilibrium in soils is presented by Valocchi (1985) who notes that basic system parameters such as flow velocity and dispersion coefficients have a significant effect on equilibria.

Due to the many potential problems with batch equilibrium experiments, and to the rather unrealistic circumstance achieved by shaking the soil particles in an aqueous solution, sorption tends to be overestimated by this technique. In an attempt to simulate actual flow conditions in the soil, miscible displacement
experiments are often used to measure the retardation \( R \) of solute movement in a soil. This is then used to obtain a value of \( K_d \) as follows:

\[
R = 1 + \frac{p_b K_d}{\theta}
\]

where \( p_b \) is soil bulk density and \( \theta \) is volumetric water content.

In these experiments, soil columns are saturated with an electrolyte solution such as 0.01 N CaCl\(_2\) or CaSO\(_4\), and a known volume of a solution of the organic compound is applied to the soil at a constant flow rate using a pump. Collection of the effluent allows measurement of the relative concentration \( C/C_0 \), which when plotted against pore volumes of solution displaced through the column \( (V/V_0) \) yields a breakthrough curve (Gamerdinger et al., 1990; Nkedi-Kizza et al., 1987; Zhong et al., 1986). Using the conservation of mass principle, it can be shown that the area above the curve is equal to \( R \), where

\[
R = \int_0^{p_{\text{max}}} 1 - C \, dp
\]

\( C \) is the relative effluent solution concentration \( (C/C_0) \), and \( p_{\text{max}} \) is the total pore volumes \( (p) \) displaced through the column (Nkedi-Kizza et al., 1987). By using carefully packed columns of soil, uniform bulk density and water content can be achieved, avoiding conditions of nonideal behavior such as preferential flow paths or macropores which might be present in undisturbed core samples (Gamerdinger et al., 1991).
Recent variations on this technique incorporate the use of two high-performance liquid chromatography pumps connected with a switching valve to the soil column. For solutes which absorb light, a flow-through variable-wavelength UV detector can be used to continuously monitor the solute concentration in the column effluent when connected to a strip chart recorder, thus simplifying the analytical process (Brusseau et al., 1990). Tritiated water is used as a conservative (non-sorbing) tracer. Desorption behavior can be measured by switching back to the electrolyte solution once $C/C_0 = 1$.

The miscible displacement technique is especially useful for low-sorptivity systems, where batch-equilibrium techniques are often inadequate. As levels of clay and organic matter increase, increasing the sorptivity of the solute, time constraints can become a problem. It may take many days to equilibrate the column prior to adding the solute, and a single breakthrough curve may take a week or longer to record. As the pumping period lengthens, the potential for degradation of the solute increases. Brusseau et al. (1990) suggest that other techniques, such as a gas-purge method often used to determine sorption of organic contaminants in sediment/water systems, may be more appropriate to use in these high-sorptivity systems.

Estimates of sorption to surfaces are essential in assessing the importance of photolysis of organic compounds in soils. Sorption of chemicals retards their movement within the soil matrix, and may physically prevent them
from reaching the light-irradiated soil surface. Sorption to clay minerals may result in surface-catalysed hydrolysis reactions, or may protect compounds from chemical attack (Graham-Bryce, 1981).

When xenobiotics become physically entrapped within soil particles, photolysis becomes unlikely due to physical light shading and absorption by the substrate. This has been referred to as the "inner filter" effect (Wolfe et al., 1990). Behymer and Hites (1985) found that fly ash stabilized photochemical degradation of polycyclic aromatic hydrocarbons, which they attributed to adsorption to carbon, the relatively low specific surface areas of the ash, or the inner-filter effect. Rates of degradation were lower on darker colored substrates, which would absorb more of the light. Yokley et al. (1986) also correlated color of the substrate to photolysis of adsorbed organic compounds, with the greatest suppression of phototransformation of pyrene and benzo[a]pyrene occurring on the darkest ashes. These researchers calculated pore sizes in the adsorbents tested, and concluded that all were sufficiently porous for an inner-filter mechanism to be active. This effect correlates with the two-site model previously described.

In other cases, sorption of xenobiotics to surfaces may result in shifts in absorbance spectra which may either enhance or retard photolysis rates (Takahashi, 1985; Jones, 1991). Likewise, sorption to surfaces may result in
quenching of photoexcited compounds via intermolecular energy transfer to humics or other substances (Hautala, 1978).

In sandy soils, where organic matter content is low, as is sorption, the extent of photolysis is often greater than is seen in loam or clay soils. Liang and Lichtenstein (1976) found that rates of photolysis of [\(^{14}\)C] azinphosmethyl were most rapid in a Plainfield sand soil, and slowest in a muck soil with 57% organic matter. The extent of photolysis decreased with increasing organic matter content. The fraction of unextractable radiocarbon also increased on the finer textured soil, suggesting that photoproducts were sorbed onto the soil organic matter. This effect was most pronounced in moist and flooded soils.

Curran et al. (1992) observed the same effect when irradiating Plainfield sand or Drummer silty clay loam soil which contained imidazolinone herbicides. Little loss was measured in the silty clay loam after exposure to UV light for 48 hours, whereas approximately 50% of imazaquin and imazethapyr were lost in moist soils. Drying of the soils resulted in reduced loss. The authors suggest that greater adsorption and reduced availability of the herbicides in the silty clay loam may account for differences in rates of photodegradation, particularly in dry soils. Dureja (1989) studied the photodecomposition of monocrotophos in four soil types and found that the rate of photodegradation was linked to the organic matter content of the soil, with the least loss observed in the soil with the highest
organic matter content. The clay content was not an accurate predictor of magnitude of loss.

e) Environmental exposure of surfaces

Soil surfaces are exposed to wide variations in environmental conditions, including diurnal and seasonal variations in temperature, changes in soil moisture content, and many land use practices. Soil surface temperatures are influenced by ambient temperatures, sunlight angles, soil albedo and reflectivity, heat capacity, and thermal conductivity. Albedo and reflectivity are a function of soil surface cover, mineral type, and organic matter content, with the typical dark color of many soils a direct consequence of organic matter (Stevenson, 1982). This dark color can enhance sunlight warming of the soil surface; however, soils which are high in organic matter content often have a higher water holding capacity, resulting in more evaporational cooling.

Two factors are important in estimating heat flux at the soil surface. Heat capacity is a function of the components of the soil mass, and can be calculated as

\[ C_{soil} = X_a C_a + X_w C_w + \sum_{j=1}^{N} X_{s_i} C_{s_i} \]

where \(X\) refers to volume fraction, \(C\) to heat capacity per volume, and the subscripts \(a, w, s_i\) to air, water and solid constituent \(i\) out of a total of \(N\) different solid materials in the soil (Jury et al., 1991). Values for the specific heat of...
various soil constituents have been tabulated, and show that the specific heat of organic matter is higher than that of soil minerals, which do not vary widely (Hillel, 1980).

The second factor, the thermal conductivity of soil, depends upon the proportions of air, liquid and solids in the matrix, the size and arrangement of the solid particles, and the degree of contact between solid and liquid phases. The ratio of thermal conductivities for quartz, water and air is 333:23:1 (Jury et al., 1991). A high air content or low water content will thus correspond to a low thermal conductivity.

Knowing these two quantities, heat flow in soils can be calculated as

$$\frac{\partial T}{\partial t} = K_T \frac{\partial^2 T}{\partial z^2}$$

where $T$ is temperature, $t$ is time, $z$ is depth, and $K_T$ is soil thermal diffusivity, or the quotient of effective thermal conductivity of the porous medium divided by soil volumetric heat capacity.

Soil temperature will be determined to a large extent by evaporation and soil cover, rather than air temperatures, although the variation in temperature with depth in soil mirrors variations in air temperatures. The periodic behavior of surface temperatures can be modeled by a sine wave whose amplitude decreases with depth. The diurnal variability in soil temperatures can affect the rate at which moisture evaporates at the surface, which can influence the transport of water soluble organics to the surface photic zone. As drying of the
soil surface proceeds, sorption will increase and retard movement of organics into this zone. Changes in soil surface temperatures will also affect compound properties such as vapor pressure and solubility, which will influence distribution coefficients.

Oxidants such as singlet oxygen which are produced on irradiated soil surfaces may result in oxidation of soil organic matter to the depth of penetration of the oxidant (<1 mm). Gohre and Miller (1983) used singlet oxygen traps to establish the production of singlet oxygen on soil surfaces. Sunlight irradiation in either an oxygen or air atmosphere was required for production of the singlet oxygen trap product. The authors speculated that the component of soil acting as a sensitizer was the organic fraction of the soil organic matter, or titanium or zinc oxides. Gohre et al. (1986) found no correlation between soil organic content and singlet oxygen reactions; instead, the greatest production of epoxides occurred on soils with lower organic matter content, suggesting that both the inorganic and organic fraction of the soil are involved in photochemical generation of singlet oxygen. Other oxidants, including peroxyl, hydroxyl, superoxide and other radicals may also be generated on soil surfaces during irradiation. Oxidations or other chemical alterations of soil organic matter will influence properties such as sorption, which would then be expected to affect photolysis rates.
f) Photolysis depths

The rates and extent of photolysis of organic compounds in soils are much slower than in distilled water (Nilles and Zabik, 1975; Allmaier and Schmid, 1985; Kulshrestha and Mukerjee, 1986). A major factor in limiting photolysis is light attenuation and screening by the soil. Both organic and inorganic chromophores limit the penetration of light into soils, with competitive light absorption greatest in the ultraviolet region (Miller and Donaldson, 1993).

In an effort to determine the effect of soil surface area on the photodecomposition of the insecticide azinphosmethyl, Liang and Lichtenstein (1976) exposed soils in beakers containing [14C] azinphosmethyl to both UV light ($\lambda_{\text{max}} = 254$ nm) and sunlight. Some of the soil treatments had 17 times larger surface area, resulting in soil depths of 1 - 1.5 mm vs. 29 mm in other treatments. More photodegradation was measured when the compound was applied to the larger surface area, suggesting that greater light absorption by the chemical was occurring due to greater surface exposure.

A series of experiments was designed to determine the depth to which light transmission occurs in soils (Hebert and Miller, 1990). Soils were treated with flumetralin and disulfoton and placed in glass petri dishes in four different soil depths, varying from 0.5 to 3.8 mm deep. Soil depth was determined by dividing the weight of soil by its bulk density and area. The soils were exposed to sunlight, with dark controls covered with black plastic. Rapid loss of
flumetralin occurred during the first three days of irradiation, with little further change in concentration with continued irradiation. It was assumed that after the third day, all of the chemical available to direct photolysis was transformed. This allowed for an estimation of the depth of photolysis by multiplying the percent recovery of starting material by soil depth when photolysis rates approached zero. Estimated photolysis depths for the direct photolysis of flumetralin varied from 0.2 to 0.6 mm in the four soils studied. Disulfoton undergoes an indirect photolysis process, and somewhat greater photolysis depths were measured for this compound, ranging from 0.4 to 1.05 mm. The mean depths were consistently greater than those measured simultaneously for flumetralin. Presumably, singlet oxygen or other oxidants may have penetrated deeper in the soil than did sunlight, allowing phototransformations to occur over greater depths.

This study demonstrated that the vertical depth of direct photolysis on soil surfaces is restricted to 0.2 - 0.3 mm, with ultraviolet light more than 90% attenuated in the top 0.2 mm of the soil profile. Depths of indirect photolysis were somewhat greater, with an estimated penetration of singlet oxygen to soil depths of 2 mm or greater depending on moisture content and soil porosity. Processes which will deliver chemicals into this photoreactive zone will thus result in increases in rates of photodegradation in soils.
IV. Model Systems for Surface Photolysis Experiments

Several reviews have been published in the last 12 years which outline model systems and light sources for assessing photodegradation of chemicals in the environment (Lemaire et al., 1982; Choudhry and Webster, 1985; Marcheterre et al., 1988; Bentson, 1990). No single effective system has yet been designed to determine rates of photolysis in soils or on plant surfaces which includes the effects of natural sunlight, varying moisture contents, soil types and depths, and transport of the compound in the experimental matrix. Various factors which must be considered in the design are presented in the following discussion.

a) Light sources

Ideally, photochemical experiments should be conducted under natural sunlight conditions. A discussion of sunlight at the earth’s surface and in water bodies is presented in Zepp and Cline (1977). However, it is often difficult to reproduce results from sunlight experiments due to daily, seasonal, and latitude variations, in addition to variability in weather conditions. Simultaneous irradiation of sunlight actinometers during the course of soil photolysis experiments can be used to estimate sunlight intensity during ambient weather conditions (Wolfe et al., 1990). When studying photolysis in soils, variations in wind speeds as well as precipitation can result in disturbance to the soil surface or loss of mass. Most outdoor experiments with soils have relied upon short
periods of irradiation during optimal weather conditions and do not give an estimation of photodegradation under more variable conditions or longer term exposure (Goetz et al., 1990; Hubbs and Lavy, 1990; Dureja, 1989; Liang and Lichtenstein, 1976).

It has instead become far more common to simulate sunlight with a number of artificial light sources. The use of artificial lights controls diurnal variability in light intensity and can maximize yields of photoproducts (Miller and Zepp, 1983). A summary of available lamps is provided by Marcheterre et al. (1988).

Filtered xenon arc lamps, such as the Hanau Suntest xenon burner, provide light which most closely matches the sunlight spectrum (Parker and Leahey, 1988). Klehr et al. (1983) used a xenon arc lamp in combination with a glass filter and solarised Duran to ensure that radiation of wavelengths less than 290 nm were absorbed. They then calculated spectral irradiance as the product of the spectral irradiance generated by the xenon arc and the transmission of the Duran and glass filter. This combination provides spectral irradiance similar to that of natural sunlight, but with three times the intensity at wavelengths up to 400 nm. Allmaier and Schmid (1985) used a mixed lamp system which included three Philips daylight lamps, one Philips UV-A lamp, and one UV-B lamp mounted in an alternate configuration which provided light of similar intensity to that of a summer's day in Vienna.
It is essential to filter out wavelengths of less than 290-295 nm, since these wavelengths do not reach the earth's surface, and can significantly alter the distribution of photoproducts. For this reason, short UV-emitting lamps such as mercury arc lamps should be avoided. The use of borosilicate glass filters to block shorter wavelength light is common, but these filters can vary individually and may emit light down to 270 nm (Miller and Zepp, 1983; Lemaire et al., 1982). For this reason, the use of optically stable filters is suggested. Chemical solution filters can be used to isolate specific wavelengths if desired (Marcheterre et al., 1988). While there has been reasonable success in mimicking the spectral distribution of sunlight, there is still no way to vary light intensity to simulate the 24 hour diurnal curve, or the changes which occur with seasons. A crude approach to simulating night and day cycles can be made by cycling the lights on and off every 12 hours. Another difficulty encountered with the use of artificial lamps is the variation of spectral intensity with distance from the lamps and position in the field (Dougherty et al., 1991).

b) Matrices: plant, soil, ash

Various substances have been used to simulate environmental surfaces, from glass slides and plates, to soils and plant leaves. A variety of plant species have been used to determine rates of photolysis of organic compounds on leaf surfaces (Lim et al., 1990; Dureja, 1989; Takahashi et al., 1985; Liang and Lichtenstein, 1976). The compound is generally applied to the leaf surface in an
organic solvent matrix using a syringe or sprayer. In these studies, rates of photodecomposition of the chemical deposited on a glass surface or in aqueous solution were determined for purposes of comparison.

Both glass surfaces and silica gel have been used as models for soils, since they are readily available, uniform, give reproducible results and are simple to use and extract. Unfortunately, neither of these surfaces resemble soil. Glass slides and plates have been used to determine surface photolysis rates by a number of researchers (Hubbs and Lavy, 1990; Goetz et al, 1990; Harrison and Thomas, 1990; Basham and Lavy, 1989). Glass surface photolysis was also used as a control in plant surface studies by Harrison and Thomas (1990) who found that rates of loss of chlorimuron and metsulfuron applied as a thin layer on glass slides were much greater than when applied to corn leaf residue. In general, rates of photolysis on glass surfaces will be more rapid than on soils, in part due to quenching by pigments in soils (Miller and Zepp, 1983).

Silica gel is not an inert substance, having a high surface reactivity and acidic properties which can result in modifications of UV absorption and emission spectra (Lemaire, 1982). Hydrogen and hydroxyl radicals formed on silica gel in the presence of light can react with organic compounds, fostering reactions and products which might not be seen on soils.

For these reasons, it is desirable to use a variety of soil types to measure photolysis reactions in soils. Choudry and Webster (1985) suggest that the soils
used should vary in organic matter content, texture (especially clay content), cation exchange capacity and pH. The pH ranges chosen should bracket the range in which pH dependent transformations are expected to occur. Soil is prepared by air-drying and sieving to the desired size, preferably large enough (1-2 mm) that soils are not greatly altered (Lemaire, 1982). Sterilization of the soil is useful in separating biotic transformations from phototransformations, although sterilization processes such as autoclaving may modify the chemical and physical properties of the soil (Saltzman and Mingelgrin, 1984). For studies involving clay minerals or humic acids, commercial products are available to ensure uniform composition (Katagi, 1991).

Studies of atmospheric photolysis reactions of compounds sorbed on ash particles have used a wide variety of substances, including silica gel, alumina, fly ash and carbon black (Behymer and Hites, 1985). This allows assessment of the dependence of photolysis processes on the nature of the surface. Silica gel and alumina have a relatively large surface area as compared to fly ash and carbon black, allowing for greater chemical dispersion, which may enhance rates of photodegradation. Likewise, variations in color may be linked to variations in rates, with rates decreasing on darker substrates which absorb more incident light (Yokley et al., 1986; Korfmarcher et al., 1980). Yokley et al. (1986) found that the source of the coal from which the ash was generated governed the degree to which polycyclic aromatic hydrocarbons were phototransformed when
adsorbed to these particles. Ash which contained greater than 10% iron and/or 0.5% carbon inhibited photolysis of both pyrene and benzo[a]pyrene; however, pH of the surface did not affect the reactions. Use of a wide variety of types of ash is thus necessary.

c) Model systems

A review of photodegradation on foliage was presented by Bentson (1990) who notes that most studies of photodegradation on foliage are performed outdoors, rather than in microcosm studies. This has made it difficult to quantify the effect of volatilization or other degradative pathways which could be important in the dissipation or degradation of organic compounds. The most common system which is used to measure photodegradation on plants consists of application of chemicals to plant leaf surfaces, with the plants being exposed to sunlight for short periods. Residues are analyzed via tissue homogenization and extraction (Dureja, 1989; Takahashi, 1985).

This method does not allow separation of the fraction still present on the leaf surface from that within the plant tissue. Studies using radiolabeled compounds show that large amounts of pesticide residues may become bound in plants via adsorption into plant tissues (Bentson, 1990). Residues in tissues are unlikely to photodegrade due to the screening effect of epicuticular waxes and intervening tissues. Another flaw of many plant photolysis studies is failure to measure sunlight intensities. Dark controls, which are physically covered to
eliminate light for a short period of time are maintained at different temperatures than outdoor, irradiated treatments. It is thus difficult to separate the effects of photodegradation from other loss processes.

No system has yet been developed which adequately simulates environmental conditions in soils which may affect photodegradation, such as varying depths, changes in moisture contents, leaching and evaporation, and diurnal variations in sunlight intensities (Parlar, 1990). The majority of research to date has used thin soil layers or slurries applied to a glass plate or petri dish and held at a constant moisture content, generally air-dry (Goshal et al., 1992; Lee et al., 1990; Basham and Lavy, 1987; Kulshrestha and Mukerjee, 1986; Burkhard and Guth, 1979). The thin layers are prepared by dipping the glass surface in a soil/water slurry and allowing the water to evaporate, or using a thin layer chromatography plate spreader, or by placing the slurry in a petri dish or beaker and allowing moisture to evaporate. When the chemical of interest is applied in a solvent matrix, penetration into soil particles may be greater than occurs under environmental conditions (Miller and Crosby, 1983).

Dark controls can be covered by aluminum foil, black plastic, or other light-blocking substances. The preparations are then irradiated either using sunlight, or by some form of artificial lamps. Some researchers have used a Rayonet merry-go-round reactor to eliminate the variation in light intensity with position (Goshal et al., 1992; Pusino and Gessa, 1991). Temperature control
can be achieved via a constant circulation water bath, and volatile compounds can be trapped if a closed system is used (Parker and Leahey, 1988; Klehr et al., 1983). Soil thin layers are useful only in determining the initial rate of surface loss of the compound under the specific conditions studied.

In thin-layer soil systems, the effect of changes in soil moisture contents on transport and photolysis of organic compounds is ignored. Liang and Lichtenstein (1976) investigated the effect of varying soil moisture content on the photodegradation of [14C] azinphosmethyl by maintaining soils in beakers at dry, field moist and flooded conditions during irradiation. Goshal et al. (1992) studied the photodegradation of pentachlorophenol in soil films in sealed systems, with moisture maintained at 20, 40 or 60%. No difference in loss was seen among any of the light-irradiated treatments. In a similar experiment with thin soil layers maintained at constant water potentials, Goetz et al. (1990) found that rates of degradation of imazethapyr increased as soil moisture increased. Hubbs and Lavy (1990) studied the upward transport of norflurazon in a soil column which was lined with filter paper and placed in beakers containing a constant water level, allowing continual upward transport and evaporation from the soil. The columns were not irradiated; instead, photolysis was measured using soil-coated and uncoated glass slides. Kieatiwong et al. (1990) used thin soil layers with added solvent to measure mobilization of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) to the irradiated soil surface.
Dougherty et al. (1991) attempted to model the effect of a porous light barrier on rates of transport and photolysis of TCDD in aqueous solution. They prepared glass cylinders with glass fiber filters which were supported below the top of the cylinder. A solution of TCDD was placed below the filter, and the solution depth was then adjusted to 2 mm above the filter. The filter blocked light but did not impede diffusion of TCDD to the surface. This system was an attempt to model both transport and light screening processes which might occur in soils.

More recently, Miller and Donaldson (1994) described a system in which cylinders of soil amended with napropamide were supplied with water from the bottom, with a constant water table depth maintained in the capillary fringe region to approximate saturated flow. These cylinders were irradiated with artificial lights, along with other cylinders of soil which were kept in an air-dry condition. This allowed both determination of rates of upward transport and the effect of transport upon rates of photodegradation in both dry and wet soil. A similar system could be adapted for use in sunlight, with variations in soil moisture contents determined by the depth to water table.

Studies of photochemical transformations on ash surfaces in the vapor phase can be performed using rotary quartz cells, vapor diffusion cells, or fluidized-bed adsorption apparatus combined with the desired lamp source (Korfmacher et al., 1980; Behymer and Hites, 1985; Yokley et al., 1986).
Fluidized-bed reactors suffer from difficulties associated with agglomeration of ash particles and a tendency for the particles to adhere to the cell walls. It is essential in these experiments to eliminate the effects of wall sorption or catalysis.

V. Modeling Photodegradation in Soils

Recent approaches to the modeling of transport and degradation of organic chemicals in soils are presented in Jury and Fluhler (1992), Hutson and Wagenet (1993), Boesten and van der Linden (1991), Wagenet and Rao (1990), Brusseau and Rao (1990), Jury et al. (1987) and Addiscott and Wagenet (1985). Traditional models for the movement and degradation of solutes in soils apply the classical convection-dispersion equation. For transient fluid flow, this can be expressed as:

\[
\frac{\partial (\theta Rc)}{\partial t} = \frac{\partial}{\partial x} \left( \theta D \frac{\partial c}{\partial x} - qc \right) - \mu \theta c
\]

where \(c\) is the volume-averaged solution concentration, \(\mu\) is a first-order decay coefficient for degradation, \(q\) is the volumetric water flux, \(x\) is distance, and \(D\) is the dispersion coefficient (van Genuchten and Wagenet, 1989).

Approaches which include two-site or two-region sorption models are presented in van Genuchten and Wagenet (1989). These models assume that degradation can be modeled as a single first order degradation rate, which is presumed to be due primarily to microbial degradation. Alternatively, two decay
coefficients, one of which applies to liquid phase concentrations and one to sorbed phase concentrations, may be used where

\[
\frac{\partial (\theta c)}{\partial t} + \rho_b \frac{\partial s}{\partial t} = \frac{\partial}{\partial x} \left( \theta D \frac{\partial c}{\partial x} - q_c \right) - \mu_t \theta c - \mu_s \rho_b s
\]

where \( s \) is the sorbed concentration, \( \mu_t \) is a first order decay coefficient for degradation from the liquid phase, and \( \mu_s \) is a first order sorbed phase degradation coefficient. This equation is valid when sorption is either an equilibrium or a kinetic process. Required data includes soil moisture characteristic curves, which describe the variation in volumetric water content with soil water potential, and estimates of chemical volatility such as Henry's Law constant.

While this approach provides a means for modeling the decay rates of different phases, it does not distinguish among chemical, photochemical, or biological mechanisms, nor does it include changes in rates which occur with changes in depth in the matrix or in soil temperature. Likewise, the parameters \( \mu_t \) and \( \mu_s \) are difficult to identify.

There are fundamental differences between transport characteristics in laboratory experiments as compared to those which are present in the field environment due to heterogeneity of field soil properties and preferential flow paths (Jury and Fluhler, 1992). Very few field scale studies exist to evaluate solute adsorption behavior in soils, and most studies have investigated pesticide residues only at shallow depths. Laboratory estimates of sorption tend to
underestimate field mobility, since these estimates neglect spatial variability and variations in porosities and flow paths (Jury et al., 1986).

Current fate models also do not incorporate decay constants for photodegradation, nor do they consider the effect of chemical formulations or dissolved organics on sorption and degradation (Wagenet and Rao, 1990). Additives such as surfactants can increase solubilization or decrease sorption of organic compounds in soils, increasing their mobility (Scheunert, 1992).

Harrison and Thomas (1990) found that adding surfactants to chlorimuron applied to glass surfaces resulted in solubilization effects and partitioning into the hydrophobic interior of the surfactant micelles. The authors speculate that some photonucleophilic effects are more favorable in the micelles than in the aqueous phase, resulting in increased rates of photolysis. Surfactants have also been shown to decrease rates of photolysis (Thomas and Harrison, 1990).

Application methods will also influence rates of photodegradation in soils. Surface application results in the most rapid rates of loss. Incorporation of chemicals into the top 5 cm of soil results in far greater persistence (Walker et al., 1985). Models will not be successful in predicting rates of loss of xenobiotics until all these factors have been included.

Perhaps the most important consideration is the rate at which the compound reaches the photic zone. For compounds which are relatively volatile, loss will be controlled by the rate of diffusion through the soil and the rate of loss
from the soil surface. For low volatility, high solubility compounds, movement upward with evaporating water can result in concentration at the soil surface, enhancing rates of photodegradation (Spencer, 1987). Diffusion in the top few millimeters of the soil will then control the amount of time during which the chemical is found within the irradiated zone in which photochemical transformations may occur.

It becomes apparent that photodegradation of xenobiotics will not be modeled successfully until these basic chemical and transport processes at the soil surface are better understood. Models must incorporate the photochemical behavior of the compound; soil texture, structure and surface color; application method; water content; advection, volatilization and sorption; and the effects of soil surface treatment and exposure. A first approach to the problem is presented by Boesten and van der Linden (1991) who describe the rate of transformation of pesticides in soils with a first-order rate equation

\[ R_t = k c^* \]

where \( R_t \) is the rate of transformation of the pesticide in the soil, \( c^* = \theta c + \rho_b X \); \( X \) is the content of pesticide sorbed, and \( k \) is the rate coefficient for transformation. Further,

\[ k = f_T f_\theta f_z k_{ref} \]

where \( f_T \) is a factor for the influence of soil temperature, \( f_\theta \) is a reduction factor for the influence of the volume fraction of liquid, \( f_z \) is a reduction factor for the
influence of soil depth, and \( k_{\text{ref}} \) is \( k \) at reference conditions. This allows the inclusion of these three factors into the calculation of the decay coefficient, which now varies with depth. A different value of \( k \) can be calculated for the top half millimeter of the soil, and the effects of changing temperatures can be included as described by Boesten and van der Linden (1991). The model also incorporates the effects of time of application on transport and degradation as well as atmospheric conditions, although volatile flux is ignored.

Until we are better able to quantify photochemical processes in soils, it seems unlikely that models will successfully predict actual photodegradative behavior of xenobiotics in the environment.

**SUMMARY**

Photolysis is the process in which absorption of light causes a transformation of the parent compound. The chemical may absorb light directly, resulting in an excited state, or another compound called a sensitizer can absorb light and then transfer energy to the chemical of interest, causing a transformation. Photochemical reactions include photooxidations, reductions, isomerizations and hydrolysis. Factors which affect rates in aqueous media include light attenuation, variations in sunlight intensity, concentration effects, and changes in the system composition.
Equations governing first-order photolysis reactions in aqueous media are well established, but they cannot be applied to photoreactions on surfaces due to a number of other mechanisms which affect rates of decomposition. Properties of surfaces which may alter photochemical reactions include soil mineral and organic fraction interactions, clay catalysis or photostabilization, metal oxide sensitization, sorption to clay or organic matter, changes in soil moisture content, physical entrapment in soil particles, environmental exposure of surfaces, and depth of light penetration in soils.

Sorption in soils governs retardation of transport, which affects rates of photolysis, and can be measured in laboratory experiments such as batch equilibrium or miscible displacement techniques. Sorption behavior of organic compounds at low concentrations is often linear, although other models may apply.

No ideal models of surfaces have yet been designed to determine photolysis rates. It is essential to use a light source such as a xenon arc lamp which produces light similar in wavelength to that of the sun. Many matrices are used to model environmental surfaces, with the most realistic results measured by using a variety of soil, ash, or plant types. Soil systems must incorporate the effect of water flux in order to realistically predict degradation rates.

Modeling of photodegradation in soils has not been successful due to the common practice of lumping all degradation processes into a single first-order
coefficient which primarily considers rates of biodegradation. Models must incorporate factors which influence the microenvironment in the top millimeter of the soil as well as upward transport processes and diffusion, which will govern chemical disposition at the soil surface.
REFERENCES


Chapter 2.

Coupled Transport and Photodegradation of Napropamide in Soils Undergoing Evaporation From a Shallow Water Table

Photolysis of pesticides at the atmosphere-soil surface interface provides one avenue by which residues are degraded. Rates of photolysis of pesticides in soil are generally slower than in distilled water, due in part to light attenuation and absorption by the soil. Organic and inorganic suspensions limit the depth of penetration of light into soil, with competitive light absorption reaching a maximum in the ultraviolet region of the spectrum, which is also the region of high solar aerosol efficiency in mediating phototransformations (1).

Rates of photolysis in soil are often measured using thin, dry sections or glass slides or in petri dishes, neglecting both the effect of depth of soil and partitioning to active photolysis processes and the effect of measured processes ultimately transferring compounds into the photically active zone.
Photolysis in soils is effectively limited to the top 0.5 mm of the soil surface. The effect of upward transport in translocating napropamide [2-(α-naphthoxy)-N,N-diethylpropionamide] into the photic zone was examined using an experimental system in which soils were supplied with water at their base. Sunlight photolysis rates were much greater than predicted if photolysis had been limited to the soil surface, with up to 70% lost in a loamy sand soil after 14 days of irradiation, as compared to dark controls. Rates of loss were slower in a sandy clay loam, with 29% loss over 14 days. Rates of transport to the surface were affected by sorption, with measured values of the distribution coefficient $K_d$ of 0.4 to 0.72 and 6.6 to 7.2 mL/g in loamy sand and sandy clay loam soils, respectively. Once the chemical has been transported to the surface, the rate of downward diffusion determines the amount of chemical in the irradiated zone.

**Introduction**

Photolysis of pesticides at the atmosphere-soil surface interface provides one means by which residues are degraded. Rates of photolysis of pesticides in soils are much slower than in distilled water, due in part to light attenuation and screening by the soil. Organic and inorganic chromophores limit the depth of penetration of light into soils, with competitive light absorption reaching a maximum in the ultraviolet region of the spectrum, which is also that region of light which is most efficient in mediating phototransformations (1).

Rates of photolysis in soils are often measured using thin, dry soil films on glass plates or in petri dishes, neglecting both the effect of depth of light penetration on active photolysis processes and the effect of transport processes which may translocate compounds into the photically active zone.
Hebert and Miller (2) measured photolysis depths in four soil types for flumetralin, which undergoes direct photolysis, and disulfoton, which undergoes indirect photolysis by reaction with singlet oxygen. Thin soil layers, from 0.5 to 3.8 mm, containing uniform concentrations of pesticides, were irradiated in sunlight and under artificial lamps. Depths of photolysis at the soil surface were estimated from the percentage of compound photodegraded over a five day period. Sunlight depths of direct photolysis averaged 0.32 mm for flumetralin, and 0.62 mm for disulfoton. The greater depths were attributed to the penetration of photochemically generated singlet oxygen on the soil surface beyond the optical depth of the soils. Some pesticide was always retained in the soil, regardless of the soil depth, which was attributed to sorption. Compounds which are sorbed may be physically shaded from light (3) or may show shifts in absorption spectra which can affect photolysis rates (4,5).

The effect of solvents on the transport and photolysis of chlorinated dioxins in soils was demonstrated in another experiment by irradiating thin soil films with and without added hexadecane under an artificial light source (6). Adding hexadecane to the soils increased rates of photolysis, and photolysis was observed to occur over a longer period than was seen in dry soils without added solvent. This suggests that migration of TCDD to the irradiated surface was facilitated by the hexadecane, possibly via solubilization and transport in the hydrocarbon film.

Predicting rates of photolysis of organic compounds in soils, then, will depend on the rate of transport into the sunlight irradiated zone; the rate of diffusion out of the irradiated zone; and the rate at which photolysis occurs on the soil surface in the active zone.
Napropamide is a broad spectrum herbicide used in the control of annual grass and broadleaf weeds in many fruit and vegetable crops (7). It is applied at the soil surface for some perennial crops, or incorporated in the top 2.5 to 5 cm of the soil. Prior work has demonstrated that napropamide is lost rapidly when applied to the soil surface, with apparent first order kinetics (8). The rate of loss was correlated to the time of year during which the compound was applied, with more loss observed in June than in April. Field incorporated napropamide was not lost rapidly, with 50% of the initial activity remaining 14 weeks after application. This compares to the 50% loss observed in the first 3 weeks following surface application. Walker et al. (9) found similar behavior in the loss of field applied napropamide, with up to 75% of the applied dose lost during the first 28 days after application in June or July, and less than 25% losses following application in November to January. Losses of surface applied chemical were closely correlated with the amounts of incoming solar radiation.

Napropamide is fairly water soluble (73 mg/L at 20 °C) and has low vapor pressure (0.53 mPa at 25 °C). Based on these parameters, Jury et al. (10) predicted that napropamide would move readily to the soil surface in the presence of an evaporative flux, but would not readily volatilize from the soil surface. Instead, downward diffusion would tend to move the chemical back into the soil, with rates of diffusion increasing and rates of volatilization decreasing as volumetric water content in the soil increases.

The purpose of this study was to determine whether rates of photolysis of napropamide are increased in the presence of upward, evaporative flux in soils. The effects of sorption and retardation on transport and photolysis were also investigated.
Materials and Methods

Soils. The soils used for this study were a loamy sand, referred to as "Callahan", collected from the 0 to 50 cm depth increment at a range site in Washoe County, Nevada, and a sandy clay loam, referred to as "Montana", collected from the 0 to 30 cm depth increment 25 miles south of Plentywood, in Sheridan County, Montana. The loamy sand soil consisted of 82% sand, 10% silt and 8% clay, with a soil-solution pH of 7.3, a cation exchange capacity (CEC) of 4 mequiv/100 g and 0.3% organic matter. The sandy clay loam contained 48% sand, 24% silt and 28% clay, with a soil-solution pH of 7.9, a CEC of 10 mequiv/100 g and 1.7% organic matter. The soils were air-dried and passed through a 1-mm sieve prior to autoclaving to ensure initial sterility.

Chemicals. Napropamide (>99% pure) was purchased from Chem Service. High purity HPLC-grade solvents and reagents were obtained from Fisher Scientific. Stock solutions were prepared in methanol to 4 mg/mL, and were further diluted with methanol to give a range of standards from 0.4 µg/mL to 32 µg/mL. Stock was stored at 4 °C in amber glass vials sealed with teflon-coated septa.

Aqueous Photolysis Experiments. Rates of aqueous photolysis for napropamide were determined in midday sunlight (ca. 12:00 noon) at the beginning and end of each experiment. Stock was diluted in distilled water to 7.4 x 10^{-5} M napropamide. The solutions were placed in 25 mL borosilicate glass test tubes with teflon-lined caps, with two replicate tubes for each treatment. The tubes were placed in full sun, under clear, polyethylene plastic, and under black plastic, and were sampled at intervals of 5, 10, 20, and 30 minutes. Temperature was not controlled. Samples were placed directly in amber autosampler vials and stored at 4 °C until analyzed.
Residues were quantified by high performance liquid chromatography (HPLC) using a Hewlett Packard 1050 Liquid Chromatograph coupled with a Linear 200 UVIS Detector set at 240 nm, and a Hewlett Packard 3396A integrator. The machine was operated isocratically at 1.2 mL/min using 55:45 acetonitrile:water with 1% acetic acid as the mobile phase. The column used was a 15 cm long Supelco DB-8-LC with 4.6 mm i.d. and 5 μm packing material. Under these conditions, the retention time was 5.7 minutes. Photolytic half-lives were calculated by least squares regression of a first order plot of time vs. relative concentration.

**Soil Transport and Photolysis Experiments.** Five photolysis experiments were conducted under differing conditions as seen in Table I. Treatments included two concentrations of napropamide; two water table depths; and control of light exposure of the surface soil through a clear plastic rain shield or through black plastic (dark controls).

Napropamide in methylene chloride was added to the soils using rotary evaporation under vacuum. Homogeneity was demonstrated by extracting and quantifying a series of soil samples.

Glass cylinders 5.5 cm in inner diameter by 5.5 cm in length were constructed from glass tubing, with open tops and closed bottoms fitted with 0.5 cm glass tubing to allow water inflow from the bottom of the cylinder. Water was supplied to the cylinders via Tygon tubing attached to a water tank equipped with a float to maintain a constant water table depth. The tanks were refilled from 2000 mL Erlenmeyer flasks to allow measurement of daily water consumption.
Table I. Experimental details for napropamide soil photolysis experiments.

<table>
<thead>
<tr>
<th>Experiment # *</th>
<th>Date</th>
<th>Concentration in Soil, ug/g</th>
<th>Depth to Water Table, Callahan Soil, cm</th>
<th>Depth to Water Table, Montana Soil, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1C, 1M</td>
<td>6/1/92</td>
<td>10</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>2C, 2M</td>
<td>6/22/92</td>
<td>30</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>3C, 3M</td>
<td>6/1/93</td>
<td>10</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>4C, 4M</td>
<td>6/21/93</td>
<td>30</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>5C, 5M</td>
<td>9/7/93</td>
<td>10</td>
<td>15</td>
<td>25</td>
</tr>
</tbody>
</table>

* C = Callahan soil; M = Montana Soil

The water tanks and Erlenmeyer flasks were covered with tarpaulins to minimize temperature fluctuations. Each water tank supplied six cylinders containing a single soil subjected to a single treatment, and both soils were irradiated concurrently. Variability in water consumption was measured using individual reservoirs, and was found to be within ± 5%.

At the start of each experiment, replicate cylinders (two per treatment per soil per sampling day) were placed in foam insulated boxes 20 cm under the clear and black plastic shields (Figure 1). The water level in the cylinders was adjusted to the 4.5 cm depth in the cylinder, the inflow tube was covered by glass wool, and unamended autoclaved soil was placed atop the glass wool to a depth of 3 cm in each cylinder. Wetting of the soil was rapid. For the experiments at the 4.5 cm water table depth, amended soil was then added to each cylinder from the 3 cm depth to the top, with the weight of soil added to each cylinder recorded. In the experiments at the 15 or 25 cm water table depth,
Figure 1. Experimental design for soil transport and photolysis experiments.
the constant head tanks were first lowered to the appropriate level prior to adding the amended soil. The soil surface was loosely covered by aluminum foil to avoid wind damage until the remainder of the soil bulk became wet via capillarity, which occurred in about 15 minutes for the 4.5 cm water depth, and in 1 to 2 hours for the 15 or 25 cm water table depth.

At the same time, 4 g control samples of amended soil were weighed into test tubes, and distilled water was added to the soil samples (1.2 g to Callahan soil; 1.5 g to Montana soil). The tubes were capped and covered with aluminum foil, and were placed in the field adjacent to the soil cylinders. On each sampling day, 4 controls for each soil type were removed and taken to the laboratory for determination of extraction efficiency.

**Soil Sampling.** The duplicate soil cylinders for each soil type and each treatment were sampled on days 3, 7 and 14 of each experiment. The inflow hoses were clamped and detached from the main feeder hoses to allow their removal. Each cm of soil in each cylinder was then excavated to the 4 cm depth, with the soil from each layer placed in a petri dish to allow mixing to reach a homogeneous concentration. Following mixing, two 5 g samples were weighed into test tubes for extraction, and the remainder of the soil layer was dried at 105 °C for soil moisture determination. All soil samples were stored in the dark at 4 °C until extracted.

**Extraction and Quantification.** Soil samples were extracted using three 6 mL aliquots of methanol. For the first two extractions, the samples were sonicated for 10 minutes, followed by shaking for 1 hour in a horizontal position. After centrifuging for 5 minutes at 3000 rpm, the supernatant was filtered through Whatman 2V filter paper and collected in a conical test tube. Sonication and shaking were omitted for the final extraction, in which the soil and solvent
mixture was agitated for 30 seconds using a Kraft pulser-vortex test tube mixer. The combined extract was reduced to 3 mL under nitrogen in a 50 °C water bath. Recoveries from dry, unaged soil averaged 87% ± 3%, with declining recoveries in the aged, moist samples.

Residues were quantified by HPLC as described above. Amounts present in the samples were determined from the standard curve constructed using a range of external standards. Detector response was linear within the range of concentrations used, and the limit of detection was 5 ng/g soil. Percent of napropamide remaining in each soil layer was calculated on a mass basis relative to the amount applied, and values were normalized by the average recovery from the control samples.

Batch Equilibrium Sorption Experiments. Isotherms for napropamide were measured for each soil using the batch equilibration method (11). Four grams of soil were placed in 15 mL test tubes, and 10 mL of various concentrations (1.6, 8, 16, 24, 32 and 40 μg/mL) of napropamide dissolved in 0.01 N CaCl₂ were added to the soil. The tubes were closed with polypropylene screw caps and shaken on the reciprocating shaker for 24 hours at room temperature (T = 24 °C ± 1 °C). This time period was previously found to be sufficient for equilibration to occur, without measurable degradation (12). Following equilibration, the tubes were centrifuged. Samples of supernatant were analyzed by HPLC, as previously described. That fraction of napropamide which had been removed from the solution was assumed to be sorbed onto the soil. Four replications were made at each concentration for each soil, and solvent and soil blanks were also included at each concentration to rule out decomposition or coelution of soil peaks.
Sorption coefficients, $K_d$ (mL/g) were determined by fitting a linear model to the sorption data, such that $S = K_d C$, where $S$ and $C$ are the sorbed (µg/g soil) and solution concentrations (µg/mL), respectively, at equilibrium. Sorbed chemical was calculated by difference from the solution concentration, such that $S = (C_i - C_f) (10 \text{ mL} / 4 \text{ g})$, where $C_i =$ initial concentration, and $C_f =$ final concentration.

**Miscible Displacement Experiments.** Miscible displacement techniques described by Brusseau et al. (13) were used to estimate retardation factors for napropamide in both soils. A 27 cm long glass Michel-Miller chromatography column with a 2.5 cm maximum internal diameter and a volume of 90 cm$^3$ was carefully packed with air-dried soil to a bulk density of 1.58 g/cm$^3$ for the Callahan soil, and 1.06 g/cm$^3$ for the Montana soil. Glass filter disks were used to retain the soil material in the column and to provide distribution of the solvent across the soil surface. A 0.01 N CaSO$_4$ solution was pumped through the column using an SSI 220B HPLC pump until steady-state, water-saturated conditions were reached. The CaSO$_4$ solution was filtered through a 0.45 µm membrane filter and degassed with helium prior to use. Equilibration required 48 hours for Callahan soil, and 72 hours or longer for the Montana soil.

Following the equilibration period, the column outflow was attached directly to a flow-through, variable wavelength UV detector (Linear UVIS 200) set at 240 nm and a linear chart recorder (Linear Instruments) to continuously record outflow concentrations. A solution of 20 mg/L napropamide in 0.01 N CaSO$_4$, filtered and degassed as before, was then introduced into the column, with the pump rate set at 2 mL/min. The rate was monitored periodically by measuring the outflow.
Retardation factors were calculated based on the conservation of mass principle (14) by measuring the area above the plotted breakthrough curves, where

\[ R = \int_0^{p_{\text{max}}} 1 - C^* dp = 1 + \frac{p_b K_d}{\theta} \]

and \( R = \) retardation, \( p = \) pore volumes, \( p_{\text{max}} = \) total pore volumes displaced through the column, \( C^* = \) relative effluent solution concentration (\( C/C_0 \)), \( p_b = \) soil bulk density (g/cm\(^3\)), and \( \theta = \) volumetric water content (cm\(^3\)/cm\(^3\)).

For the Callahan soil column, volumetric water content was 0.41 and one column pore volume was 39.5 mL; for the Montana soil column, water content was 0.58 and one column pore volume was 51.8 mL of water. These values were used to calculate estimates of \( K_d \) to compare with previous estimates from batch equilibrium experiments.

**Results**

**Aqueous Photolysis Experiments.** Napropamide degraded rapidly when irradiated in sunlight. Loss via photolysis followed first order kinetics. The average sunlight photolysis half-life for June, and the accompanying rate constant, were 7.3 min and \( 9.5 \times 10^{-2} \) min\(^{-1} \), respectively (\( R^2 = 0.999 \)). Rates under the clear plastic shield were somewhat slower, with an average half-life and rate constant of 7.8 min and \( 8.9 \times 10^{-2} \) min\(^{-1} \) (\( R^2 = 0.999 \)). Slow loss of napropamide was observed in aqueous solution under the dark plastic shield, presumably due to scattered light. The average half-life and rate constant were...
124 min and $5.6 \times 10^{-3}$ min$^{-1}$ ($R^2 = 0.993$). Half lives measured in September 1993 were slower due to a reduction in sunlight, with half lives measured of 8.7, 9.7, and 233 min under sunlight, clear plastic, and dark plastic, respectively.

These values correspond well to those measured in aqueous solution exposed to simulated sunlight. Chang et al. measured a half-life for napropamide of 5.7 min, which corresponded to a natural sunlight half-life of 6.8 min, with a rate constant of $1.0 \times 10^{-2}$ min$^{-1}$.(15)

**Soil Transport and Photolysis Experiments.** Napropamide was rapidly photodegraded in the Callahan soil, with an average of $70 \pm 4.1\%$ more lost in the light-exposed soils after 14 days of irradiation in experiments 1C through 4C, as compared to the dark controls (Figures 2 and 3). Rates of photodegradation were considerably slower than those measured in aqueous solution due to the physical and chemical characteristics of the soil, with a time to reach 50% of the initial concentration of three to four days. Loss was slightly less in the September experiment (5C) due to less incoming solar radiation, with 63% more lost from the light-exposed soils (Figure 4). Distribution of napropamide with depth as seen in Figure 5 shows that upward movement of napropamide in this soil was rapid in experiments 1C and 2C, with less than 10% remaining below the top cm of soil after 3 days, due to the near-saturated soil conditions and minimal sorption.
Figure 2. Irradiation of napropamide on Callahan soil with water table at 4.5 cm. (a) 10 µg/g; started 6/1/92; (b) 30 µg/g; started 6/22/92.

□ = light-exposed; ● = dark controls.
Figure 3. Irradiation of napropamide on Callahan soil with water table at 15 cm. (a) 10 \text{ug/g}; started 6/1/93; (b) 30 \text{ug/g}; started 6/21/93.
\begin{itemize}
\item \text{□} = light-exposed;
\item \text{●} = dark controls.
\end{itemize}
Figure 4. Irradiation of napropamide on Callahan soil with water table at 15 cm. Started 9/7/93; 10 ug/g applied.

\( \text{\textbullet} \) = light-exposed; \( \text{\square} \) = dark controls.
Figure 5. Distribution of napropamide with depth in Callahan soil with water table at 4.5 cm (2C).
A gradient of less than 3% soil moisture by weight was measured in the Callahan soil cylinders from the 4 cm depth to the soil surface when the depth to water table was 4.5 cm. In the experiments in which the depth to water table was increased to 15 cm, soil moisture gradients of up to 9% were measured, and the soil surface was visibly drier. The distribution of napropamide with depth in Callahan soil when undergoing unsaturated flow (3C) is seen in Figure 6. While upward transport was still rapid in experiments 3C through 5C, rates of photolysis were somewhat slower initially, with less loss measured on days 3 and 7 in all three experiments. The time to lose 50% of the initially applied amount of napropamide was between 3 and 4 days for 1C and 2C, but almost 7 days for experiments 3C through 5C. The process does not follow first order kinetics, since total loss was similar on day 14 despite the variation in rates over the two week period.

Much less loss was measured in Montana soil, with an average of 29 ± 1.9% less in the sunlight-irradiated treatments than in the darks after 14 days for experiments 1M through 4M (Figures 7 and 8). Only 16.8% was lost in the September experiment (Figure 9). Time to lose a similar mass in the Callahan soil experiments was less than 3 days in 1C and 2C, and about 3 days in 3C through 5C. Likewise, movement upward was considerably slower, with up to 30% remaining below the top 1 cm of soil in experiments 1M and 2M, and up to 40% in experiments 3M and 4M, as shown by the distribution of napropamide with depth seen in Figures 10 and 11. There was a greater difference in surface
Figure 6. Distribution of napropamide with depth in Callahan soil with water table at 15 cm (3C).
Figure 7. Irradiation of napropamide on Montana soil with water table at 4.5 cm. (a) 10 ug/g; started 6/1/92; (b) 30 ug/g; started 6/22/92.

○ = light-exposed; ● = dark controls.
Figure 8. Irradiation of napropamide on Montana soil with water table at 25 cm. (a) 10 ug/g; started 6/1/93; (b) 30 ug/g; started 6/21/93.  
\(\square\) = light-exposed; \(\bullet\) = dark controls.
Figure 9. Irradiation of napropamide on Montana soil with water table at 25 cm. Applied 10 ug/g; started 9/7/93.

• = light-exposed; • = dark controls.

Figure 10. Distribution of napropamide with depth in Montana soil with water table at 4.5 cm (2M).
Figure 10. Distribution of napropamide with depth in Montana soil with water table at 4.5 cm (2M).

Montana soil with water table at 4.5 cm (2M).

Depth in Soil (cm)
Figure 11. Distribution of napropamide with depth in Montana soil with water table at 25 cm (3M).
soil moisture, with a gradient of only 3 to 8 percent in the top 4 cm of soil when
the depth to water table was 4.5 cm, and a gradient of up to 22% moisture by
weight when the water table depth was 25 cm.

Average daily evaporative flux is presented in Table II. Water flux was
similar in both Callahan and Montana soils under near saturated flow conditions
(experiments 1 and 2) reflecting the shallow water table, with flux regulated by
the boundary layer above the soil surface and environmental conditions. Flux
was always less in the dark controls due to shading of the soil surface, which
reduced soil and air temperatures. Flux generally decreased as the depth to
water table increased, although it must be noted that the weather was cool,
moist and cloudy during the entire first week of experiment 3, and cool as well
during 5, which affected evaporative demand.

Table II. Average daily evaporative flux in Callahan and Montana soils.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Callahan Soil</th>
<th>Montana Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Light-exposed</td>
<td>Dark Controls</td>
</tr>
<tr>
<td>1C, 1M</td>
<td>1.47</td>
<td>1.24</td>
</tr>
<tr>
<td>2C, 2M</td>
<td>1.57</td>
<td>1.25</td>
</tr>
<tr>
<td>3C, 3M</td>
<td>1.01</td>
<td>0.72</td>
</tr>
<tr>
<td>4C, 4M</td>
<td>1.47</td>
<td>1.09</td>
</tr>
<tr>
<td>5C, 5M</td>
<td>0.97</td>
<td>0.67</td>
</tr>
</tbody>
</table>

* C = Callahan soil; M = Montana Soil
**Batch Equilibrium Experiments.** Data from the batch equilibrium experiments fit the linear model well, with 10 times as much sorption measured in Montana soil as compared to Callahan soil (Figure 12). Calculated values of $K_d$ for the two soils were 0.72 mL/g (Callahan soil, $R^2 = 0.996$) and 7.2 mL/g (Montana soil, $R^2 = 0.999$). The increase in sorption in the Montana soil can be attributed both higher organic matter and clay content. Sorption of nonpolar organic compounds is most closely related to the organic matter content of the soil, and values of $K_d$ are sometimes expressed in terms of the fraction of organic matter in soils ($f_{om}$) such that $K_{om} = K_d / f_{om}$ (16). More frequently, values in the literature are reported as $K_{oc}$, or $K_d / f_{oc}$, where $f_{oc}$ is the fraction of organic carbon in the soil. Values of $K_{om}$ are 241 and 424 mL/g for Callahan and Montana soils, respectively. These values suggest that organic matter is indeed responsible for much of the sorption observed.

**Miscible-Displacement Experiments.** Breakthrough curves for napropamide in both soils are presented in Figure 13. Napropamide moved through the Callahan soil column much more rapidly than through Montana soil, as expected from the results of the batch equilibrium experiments. Values of $R = 2.62$, $K_d = 0.4$, and $K_{om} = 133$ mL/g were estimated from the Callahan soil curve. Breakthrough in the Montana soil was greatly retarded. Values of $R = 12.2$, $K_d = 6.6$, and $K_{om} = 388$ mL/g were calculated from the measured curves.

Estimates of sorption in both experimental soils are similar to those measured by other researchers. Gerstl and Yaron (18) measured sorption of napropamide in 6 different soils, with values of $K_d$ between 0.27 and 3 mL/g and $K_{oc}$ from 249 to 450 mL/g. Elabd et al. (12) measured $K_d$ in columns of undisturbed field soil, with mean estimates of $K_d$ from batch and column
Figure 12. Batch equilibrium sorption of napropamide on two soils.
Figure 13. Breakthrough curves for napropamide on two soils.
experiments of 2.01 mL/g ± 31% and 1.91 mL/g ± 26%. This translated to $K_{oc}$ values of 363 and 333 mL/g for batch and column sorption experiments, respectively. Jury et al. (10) used a value of $K_{oc}$ of 300 for applying a pesticide screening model to evaluate transport and degradation potential. Lower estimates of $K_d$ from the miscible-displacement experiments are probably due to immobile zones within the soil flow path in the column, and may more accurately reflect the degree of sorption occurring in the soil cylinders.

**Discussion**

Reported half-lives for degradation of napropamide in soils range from 34 to 201 days, depending on temperature and moisture content (17). When incorporated into the soil bulk, half-lives of 130 to 200 days were measured, with 25% remaining after 12 months (9). The predominant mode of degradation was assumed to be microbial.

The data presented, however, have shown that when a mechanism is present to translocate the compound into the photic zone, rates of loss are greatly accelerated, with the time to reach 50% of the initially applied amount of napropamide ranging from ≈ 4 to 23 days depending on soil type. These rates are conservative due to the presence of the plastic rain shield, and represent average rates of photodegradation for midsummer weather conditions.

The loss of napropamide from the dark soil treatments, similar to that seen in the aqueous photolysis experiment, is presumed to be due to light scatter under the dark plastic shield. It is also possible that some microbial degradation is occurring by 14 days in these initially sterilized soils. While volatilization could also account for some of the loss from the dark controls, an estimate of Henry's constant ($K_H$) for napropamide of $7.9 \times 10^{-7}$ suggests that
volatilization is a minor loss pathway (18). By expressing the data in terms of the difference between the amounts present in the dark controls and the light-exposed soils, the dominant mechanism of loss seen in the experiments can be attributed to photolysis.

The rapid rate of photodegradation of napropamide measured, with up to 70% lost from the loamy sand soil in 14 days, has profound implications not only on the application and persistence of agricultural compounds, but also on the fate of chemicals at contaminated sites. Photolysis of photolabile water-soluble compounds will be maximized in coarse textured soils, and will decline relative to the amount of sorption and retardation of evaporative transport. Defining soil parameters which relate to sorption and transport will be essential in estimating the degree of photolysis which is expected to occur.

If photolysis is assumed to be limited to the top 1 mm of the soil, in the absence of transport mechanisms only 1/30th of the applied compound (1 mm in 3 cm) would be expected to photodegrade in the amended soil. The rate at which the compound reaches the soil surface, then, will determine how much chemical is available to undergo photolysis. This rate will be governed by the evaporative flux, sorption and retardation, and the volumetric water content of the soil. An estimate of the time it would take to move 3 cm in the soil is:

\[ t_c = \frac{1}{V_E} \]

where \( t_c \) = the convection time to move a distance / when a water flux \( J_W \) is present, and

\[ V_E = J_W / ( \rho_b K_d + \theta + a K_H ) . \]
$V_E$ is the convective velocity, or the ratio of water flux to concentration in the liquid phase, and $a$ is the volumetric air content (18). In a similar manner, a characteristic diffusion distance $l_d$ for napropamide at the soil surface can be calculated as

$$l_d = \frac{D_E}{J_W}$$

where $J_W$ is the evaporation rate and $D_E$ is the effective soil diffusion coefficient, which is given in Jury et al. (19) as

$$D_E = \frac{D_{G}^{\text{air}} K_H a^{10/3} / \phi^2 + D_{L}^{\text{water}} \theta^{10/3} / \phi^2}{\rho_b K_d + \theta + a K_H}$$

where $D_{G}^{\text{air}}$ is the gaseous diffusion coefficient in air, $D_{L}^{\text{water}}$ is the liquid diffusion coefficient in water, and $\phi$ is porosity. Once the compound has reached the soil surface, the rate of diffusion into and out of the sunlit zone will affect rates of photolysis.

Based on the parameters listed in Table III, calculations of $t_c$ and $l_d$ were made for both soils and both water table depths. Estimates are conservative, using the larger values of $K_d$ from the batch equilibrium experiment, and the lower rates of water flux in experiment 3 for the greater depth to water table experiments (Table IV). Under unsaturated flow conditions, the convective travel time increases, indicating that transport of water soluble compounds will be most rapid under saturated flow conditions, and will become slower as $\theta$ approaches...
Table III. Soil and chemical parameters used in calculation of \( t_c \) and \( l_d \).

<table>
<thead>
<tr>
<th></th>
<th>Callahan Soil</th>
<th>Montana Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Light-exposed</td>
<td>Dark controls</td>
</tr>
<tr>
<td>( l ) (m)</td>
<td>.03</td>
<td>.03</td>
</tr>
<tr>
<td>( t ) (days)</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>( J_w ) (m/d), water table at -4.5 cm (^a)</td>
<td>0.015</td>
<td>0.0125</td>
</tr>
<tr>
<td>( J_w ) (m/d), water table at -15 or -25 cm (^b)</td>
<td>0.0101</td>
<td>0.0072</td>
</tr>
<tr>
<td>( K_d ) (m(^3)/kg)</td>
<td>7.2 ( \times 10^{-4} )</td>
<td>7.2 ( \times 10^{-4} )</td>
</tr>
<tr>
<td>( \rho_b ) (kg/m(^3))</td>
<td>1450</td>
<td>1450</td>
</tr>
<tr>
<td>( \theta ) (m(^3)/m(^3)), water table at -4.5 cm (^c)</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>( \theta ) (m(^3)/m(^3)), water table at -15 or -25 cm (^c)</td>
<td>0.37</td>
<td>0.37</td>
</tr>
<tr>
<td>( a ) (m(^3)/m(^3)), water table at -4.5 cm (^c)</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>( a ) (m(^3)/m(^3)), water table at -15 or -25 cm (^c)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>( D_{S_{\text{air}}} ) (m(^2)/d) (^d)</td>
<td>4.3 ( \times 10^{-1} )</td>
<td>4.3 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>( D_{S_{\text{water}}} ) (m(^2)/d) (^d)</td>
<td>4.3 ( \times 10^{-5} )</td>
<td>4.3 ( \times 10^{-5} )</td>
</tr>
<tr>
<td>( \phi ) (m(^3)/m(^3)) (^c)</td>
<td>0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>( K_{\text{wa}} ) (dimensionless) (^d)</td>
<td>7.90 ( \times 10^{-7} )</td>
<td>7.90 ( \times 10^{-7} )</td>
</tr>
</tbody>
</table>

\(^a\) Values from average of experiments 1 and 2

\(^b\) Values from experiment 3

\(^c\) Values obtained from soil moisture characteristic curve, \( \theta \) vs hydraulic head in cm (data not shown)

\(^d\) From Jury et al. (10)
Table IV. Estimates of convection time to move napropamide a distance of 3 cm, and characteristic diffusion distance for 14 days.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Depth to water table = 4.5 cm</th>
<th>Depth to water table = 15 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Light-exposed</td>
<td>Dark controls</td>
</tr>
<tr>
<td>Callahan Soil</td>
<td>2.9</td>
<td>3.4</td>
</tr>
<tr>
<td>$t_c$ (days)</td>
<td>.053</td>
<td>.064</td>
</tr>
<tr>
<td>Montana Soil</td>
<td>Depth to water table = 4.5 cm</td>
<td>Depth to water table = 25 cm</td>
</tr>
<tr>
<td>$t_c$ (days)</td>
<td>16.3</td>
<td>19.4</td>
</tr>
<tr>
<td>$l_d$ (cm)</td>
<td>.016</td>
<td>.019</td>
</tr>
</tbody>
</table>

zero, unless evaporative flux rates remain high. Diffusion distances will be at a maximum when soil is saturated, with distances decreasing as $\theta$ approaches zero.

The difference in convective transport between the two soils, which can be attributed primarily to the difference in sorption coefficients, is useful in explaining the variation in rates of loss of napropamide which were measured in the soil transport experiments. In Callahan soil, the rate of transport to the surface was rapid, but a greater depth of downward diffusion out of the photic zone likely occurred as compared to that estimated for the Montana soil. The relationship between the rates of loss, then, cannot be explained simply on the basis of variations in sorption distribution coefficients. Results from the experiments at both water table depths in the Montana soil were sufficiently similar that differences in photolysis over the 14 day period cannot be related only to convective travel time, which would predict much slower movement to the soil surface in the drier soils, and thus slower rates of photolysis. Other soil
properties, such as surface color and albedo, reaction quenching, and surface pore sizes, tortuosity, and diffusion, will also have a large effect on rates of photolysis, as will soil thermal gradients which affect rates of vapor transport.

**Conclusions**

Rates of photolysis of organic compounds in soils are determined by the amount of compound which is present within the sunlight irradiated zone. The results of these experiments demonstrate that transport of water soluble compounds with evaporating water can have a substantial effect on the rate of photodegradation of these chemicals. This has implications for methods of field application of pesticides and timing of irrigation to maximize the effectiveness of the pesticide. The method may also be of use in remediating contaminated areas containing compounds which are photolabile, and which can be subirrigated. Under field conditions, however, the magnitude of the effect will be limited by the rate at which the compound is translocated to the surface, which will be relatively slow in unsaturated soils or where the depth to water table is great. If rapid flux rates can be maintained as volumetric water content drops, rates of transport will be maximized. Modeling of this process, however, will not be effective until more is understood about the mechanisms of photolysis at soil surfaces.

**Registry Number:** Napropamide, 15299-99-7.
Literature Cited


Acknowledgment

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Chapter 3.

Photolysis of Imazaquin in Soils Subject to an Evaporative Flux

INTRODUCTION

Field-applied chemicals are subject to weathering, processes such as
leaching, plant uptake, volatilization, and soil processes, as well as
photolysis processes. Several studies investigated chapters of
photolysis.
ABSTRACT

Photodegradation of imazaquin (2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolinecarboxylic acid) was measured in two soils to determine the effect of transport upward with evaporating water on rates of loss. Columns containing imazaquin homogeneously incorporated in loamy sand or sandy clay loam soils were irradiated in ultraviolet (UV) light ($\lambda_{\text{max}} = 310$ nm) or sunlight for up to 14 days. Water was applied to the base of the columns and allowed to move imazaquin upward to the irradiated surface. The rate of loss of imazaquin was increased substantially in both soils relative to controls. Up to 58% greater loss was observed following irradiation of the loamy sand soil, and up to 31% increased loss in the sandy clay loam soil. Little change was seen in dry soils exposed to constant UV irradiation, with only 7.5% less after 9 days. Measured sorption in these soils was very low with essentially no retardation occurring, allowing both upward convective flux and downward diffusion to occur. These results show that the photolysis of imazaquin can be increased substantially by movement upward with evaporating water.

INTRODUCTION

Field applied herbicides are subject to transfer processes, such as leaching, plant uptake, volatilization, or soil adsorption, as well as transformation processes, which include microbial, chemical or photochemical degradation.
The magnitude of the various effects will depend upon the chemical and physical properties of the herbicide and environmental conditions including soil moisture and temperature, soil properties, and cultural practices. For herbicides which susceptible to photolysis at the soil surface, the method of application has a significant effect on persistence. Likewise, soil properties which govern sorption in soils, especially the organic matter and clay content, will greatly affect persistence and photodegradation.

Imazaquin is an imidazolinone herbicide used for broadleaf weed control in soybeans and other legume crops. Field persistence has been shown to result in injury to corn, cotton and other crops planted one year later (Barnes et al., 1989; Loux et al., 1989a; Mills and Witt, 1989; Renner et al., 1988). The method of application, whether pre-emergence surface application or pre-plant incorporation, as well as the timing of rain or irrigation following application, have been found to affect persistence (Renner et al., 1988; Basham et al., 1987a). Incorporation into the soil bulk was shown to reduce the rate of loss, while loss of surface-applied imazaquin was rapid in hot, dry weather conditions. Dissipation was rapid during the first 30 days following application, with a decrease in rate of loss over the next four months.

Biodegradation has been shown to be a significant contributor to loss of soil-applied imazaquin. Basham and Lavy (1987b) found that the most rapid loss occurred when soils were held at warm and moist conditions which were
conducive to microbial growth. Half-lives based on corn bioassay ranged from 1.3 to 11.7 months, depending on the soil type and the environmental conditions. Dissipation was faster in a silt loam soil than in a silty clay, presumably due to greater adsorption in the latter. Cantwell et al. (1989) found that rates of biodegradation of imazaquin were dependent on soil type, with adsorption of herbicide being negatively correlated with degradation. They deduced that the amount of microbial degradation was determined by the amount of herbicide in the soil solution.

Imazaquin coated on glass slides or on thin soil layers is rapidly photodegraded, with greater loss in sunlight as compared to artificial ultraviolet (UV) light (Basham and Lavy, 1987a). When imazaquin was exposed to UV light in aqueous solution, 100% was degraded after 48 hours (Curran et al., 1992). In moist sand, 45% of applied imazaquin was lost after 48 hours, but less than 10% was lost when applied to air dry sand (Curran et al., 1992). For the soil experiments, sealed dishes were used to maintain soils at constant moisture levels throughout the experiment. Microbial degradation was ignored due to the rapid time frame of these experiments.

Soil photolysis experiments performed in sealed systems or on thin soil layers ignore the effects of transport on rates of photodegradation. Upward movement of herbicides in subirrigated columns under laboratory conditions can be significant as a result of capillarity and evaporative flux (Hubbs and Lavy,
1990). Since photolysis is limited to the top 0.5 mm of the soil surface, due to physical light shielding and attenuation by the soil (Hebert and Miller, 1990), processes which move chemicals into this surface zone may enhance rates of photolysis.

The pK\textsubscript{a} of the carboxylic acid group of imazaquin is 3.8 (Worthing and Hance, 1991), and the herbicide should primarily be anionic at the pH of most agricultural soils. Non-specific sorption can thus be expected to be minimal, with convective flux rates approaching those of unretained solutes. Increasing amounts of irrigation increased leaching of imazaquin in field soils, with maximal movement when the weather is cool and wet following application (Basham et al., 1987b). With a solubility of 60 mg/L of water at 25 °C (Worthing and Hance, 1991), most of the imazaquin present in soils should be in the soil solution, and should move up readily with evaporating water. Volatilization, on the other hand, is expected to be a minor loss pathway, due to a vapor pressure of <0.013 mPa at 60 °C (Worthing and Hance, 1991). The objective of this research was to determine the magnitude of increase in rates of photodegradation of imazaquin in soils which are subjected to evaporative flux in the presence of both sunlight and UV light.
MATERIALS AND METHODS

Soils. The soils used for this study were a loamy sand, referred to as "Callahan", collected from the 0 to 50 cm depth increment at a range site in Washoe County, Nevada, and a sandy clay loam, referred to as "Montana", collected from the 0 to 30 cm depth increment 25 miles south of Plentywood, in Sheridan County, Montana. Soil parameters are presented in Table 1. The soils were air-dried and passed through a 1-mm sieve prior to autoclaving for 45 minutes to ensure initial sterility.

Table 1. Characteristics of soils used in photolysis experiments.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>% organic matter</th>
<th>% sand</th>
<th>% silt</th>
<th>% clay</th>
<th>cation exchange capacity (mequiv 100 g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Callahan soil</td>
<td>7.3</td>
<td>0.3</td>
<td>82</td>
<td>10</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Montana soil</td>
<td>7.9</td>
<td>1.7</td>
<td>48</td>
<td>24</td>
<td>28</td>
<td>10</td>
</tr>
</tbody>
</table>

Chemicals. Imazaquin (>99% pure) was obtained from the Agricultural Research Division, American Cyanamid Co., Princeton, NJ. High purity, HPLC-grade solvents and reagents were obtained from Fisher Scientific. Stock solutions of imazaquin were prepared in methanol to 4 mg/mL, and were further diluted with methanol to give a range of standards from 0.4 μg/mL to 40 μg/mL. Stock was stored at 4 °C in amber glass vials sealed with teflon-coated septa.
Aqueous Photolysis Experiments. Rates of aqueous photolysis for imazaquin were determined in midday sunlight at the beginning and end of each soil photolysis experiment. Stock was diluted in distilled water to $6.1 \times 10^{-5}$ M imazaquin. The solutions were placed in 25 mL borosilicate glass test tubes with teflon-lined caps, with two replicates for each treatment. The tubes were placed in full sun, under clear, polyethylene plastic, and under black plastic, and were sampled at intervals of 15, 30, 60, and 120 minutes. Samples were placed directly in amber autosampler vials and stored at 4 °C until analyzed.

Rates of aqueous photolysis were determined in a similar manner under UV light using 16 Westinghouse FS40 lamps ($\lambda_{\text{max}} = 310$ nm). Dark controls were covered with aluminum foil. All tubes were placed 30 cm below the lamps, with temperatures maintained at 30 °C ± 2 °C. Sampling was performed over a 4 hour period.

Residues were quantified by high performance liquid chromatography (HPLC) using a Hewlett Packard 1050 Liquid Chromatograph coupled to a Linear 200 UVIS Detector set at 254 nm. A Hewlett Packard 3396A integrator was used for peak quantitation. The HPLC was operated isocratically at 0.9 mL/min using 38:62 acetonitrile:water with 1% acetic acid as the mobile phase. The column used was a 15 cm long reversed phase Supelco DB-8-LC with 4.6 mm i.d. and 5 µm packing material. Under these conditions, the retention time was 5.4 minutes. Amounts present in the samples were calculated by dividing
the integrated peak area of the stock solution by the integrated peak area of the irradiated sample.

Photolysis half-lives were calculated using least squares linear regression of time $t$ (minutes) vs. $\ln (C_0 / C_t)$, where $C_0 =$ initial concentration and $C_t =$ concentration at time $t$. The rate constant, $k_p$, was then determined, where

$$\ln (C_0 / C_t) = k_p t$$

Half-lives for each treatment and full sunlight were then calculated as

$$t_{1/2} = \frac{\ln 2}{k_p}.$$

**Batch Equilibrium Sorption Experiments.** Isotherms for imazaquin were measured for each soil using the batch equilibration method (Rao et al., 1990). Five grams of soil was placed in 15 mL test tubes, and eight mL of various concentrations (0.8, 1.6, 4, 8, 16, and 32 pg/mL) of imazaquin dissolved in 0.01 N CaCl$_2$ were added to the soil. The tubes were closed with polypropylene screw caps and shaken on the reciprocating shaker for 24 hours at room temperature ($T = 24 ^\circ C \pm 1 ^\circ C$). This time period was previously found to be sufficient for equilibration to occur without measurable degradation (Che et al., 1992). Following equilibration, the tubes were centrifuged and samples of supernatant were analyzed by HPLC, as previously described. That fraction of imazaquin which had been removed from the solution was assumed to be sorbed onto the soil. Four replications were made at each concentration for
each soil, and solvent and soil blanks were also included at each concentration
to rule out decomposition or interference.

Sorption coefficients, $K_d$ (mL/g) were determined by fitting a linear model
to the sorption data, such that $S = K_d C$, where $S$ and $C$ are the sorbed (ug/g soil) and solution concentrations (ug/mL), respectively, at equilibrium. Sorbed chemical was calculated by difference from the solution concentration, such that $S = (C_i - C_f)(8 \text{ mL} / 5 \text{ g})$, where $C_i =$ initial concentration, and $C_f =$ final concentration.

**Miscible Displacement Experiments.** Miscible displacement techniques described by Brusseau et al. (1990) were used to estimate retardation factors for imazaquin in both soils. The column used was a 27 cm long glass Michel-Miller chromatography column with a 2.5 cm maximum internal diameter and a volume of 90 cm$^3$. The column was carefully packed with air-dried soil to a bulk density of 1.5 g/cm$^3$ for Callahan soil, and 1.05 g/cm$^3$ for Montana soil. Glass filter disks were used to retain the soil material in the column and to spread the solvent across the soil surface. A 0.01 N CaSO$_4$ solution was pumped through the column using an SSI 220B HPLC pump until steady-state, water-saturated conditions were reached. The CaSO$_4$ solution was filtered through a 0.45 μm membrane filter and degassed with helium prior to use. Equilibration was reached in 48 hours for Callahan soil, and 72 hours or longer for the Montana soil.
Once equilibrated, the column outflow was attached directly to a Linear UVIS 200 flow-through, variable wavelength UV detector set at 254 nm, which was connected to a Linear Instruments chart recorder to continuously record outflow concentrations. A filtered and degassed solution of 20 mg/L imazaquin in 0.01 N CaSO₄ was then introduced into the column at a pump rate of 2 mL/min. The rate was verified periodically by measuring the outflow. Once the outflow concentration equaled the inflow concentration (or C/C₀ = 1), the imazaquin was desorbed from the soil column using 0.01 N CaSO₄.

Retardation factors were estimated based on the conservation of mass principle (Nkedi-Kizza et al., 1987) by calculating the area above the plotted breakthrough curves, where

\[ R = \int_0^{p_{\text{max}}} 1 - C^* \, dp = 1 + \frac{\rho_b K_d}{\theta} \]

and R = retardation, p = pore volumes, pₘₐₓ = total pore volumes displaced through the column, C* = relative effluent solution concentration, ρₐ = soil bulk density (g/cm³), and θ = volumetric water content (cm³/cm³).

For the Callahan soil column, θ was 0.43 and one column pore volume was 39.5 mL; for the Montana soil column, θ was 0.58 and one column pore volume was 51.8 mL of water. These values were used for estimating Kₐₕ for each soil.
Soil Transport and Photolysis Experiments. Three photolysis experiments were conducted to determine the effect of upward transport on rates of photolysis. A first experiment, using Callahan soil containing 15 μg/g of imazaquin, was done in the laboratory using the UV lamps (started 2/24/92). Treatments included light exposed vs. light shielded soils undergoing constant evaporation; and light exposed vs. light shielded air dry soils receiving no water.

Two more experiments were performed outdoors in sunlight, at the same concentration in both soils (started 7/13/92 and 7/13/93). Treatments for the outdoor experiments included variable flow conditions imposed by two water table depths and control of light exposure of the surface soil through a clear plastic rain shield or through black plastic (dark controls).

The sterilized soils were amended to 15 μg/g imazaquin using rotary evaporation under vacuum, with methylene chloride as the solvent. Concentrations in the soil were homogeneous, and were verified by extracting and quantifying a series of soil samples.

Indoor Experiments

For the indoor experiment, glass cylinders 5.5 cm in inner diameter by 5.5 cm in length were constructed from glass tubing, with open tops and closed bottoms fitted with 0.5 cm glass tubing to allow water inflow from the bottom of the cylinder. Distilled water was supplied to the cylinders via Tygon tubing attached to individual water reservoirs covered with parafilm and aluminum foil to
avoid evaporative loss. Reservoirs were filled daily to measure water use. Variability in water consumption measured in the individual reservoirs was within ± 5%.

At the start of the experiment, replicate cylinders (two per treatment per sampling day) were placed in foam insulated boxes in the light bank. The water level in the cylinders was adjusted to the 4.5 cm depth, the inflow tube was covered by glass wool, and unamended sterilized soil was placed atop the glass wool to a depth of 3 cm in each cylinder. Wetting of the soil was rapid. Once the soil was wet, a measured amount of amended soil containing imazaquin was placed atop the wetted soil and was allowed to wet by capillarity. The water level in the reservoirs was maintained at the 4.5 cm depth in the soil at all times to approximate saturated flow conditions. Two control cylinders were filled in the same manner, but the hoses were clamped and the soil sampled 15 minutes after the soil surface was visibly wet. This allowed determination of initial distribution of imazaquin with depth at the beginning of the experiment.

At the same time, four cylinders with sealed bottoms were filled with dry sterilized soil to the 3 cm depth, and amended soil to the surface. These cylinders received no water throughout the experiment, and were used to measure photodegradation in air dry soil. Control samples (5 g amended soil plus enough water to saturate, plus 5 g dry samples) were also weighed into
mL vials covered with aluminum foil, sealed, and placed in the light bank to monitor extraction efficiency over the course of the experiment.

Soils which were to be irradiated were placed 30 cm below the FS40 lamps used for the aqueous photolysis experiments. Dark controls were shielded from light by placing black plastic 10 cm above the soil surface. This allowed evaporation to occur in the absence of light. Constant air flow across the soils was maintained by a series of fans, and temperatures were 30 °C ± 2 °C. The soils were irradiated constantly for up to 9 days.

Outdoor Experiments

The design of the outdoor experiments was similar, with the same glass cylinders used, but both soils were irradiated simultaneously. All the cylinders for a given treatment were supplied with distilled water from a tank equipped with a float to maintain a constant water table depth. The constant head tanks were refilled daily from 2000 mL Erlenmeyer flasks. The water tanks and Erlenmeyer flasks were covered with tarpaulins to minimize temperature fluctuations.

At the start of each outdoor experiment, replicate cylinders (two per treatment per soil per sampling day) were placed in foam insulated boxes 20 cm below the clear and black plastic shields (Figure 1). For first outdoor experiment, the water table was maintained at the 4.5 cm depth in the soil, for near-saturated flow conditions. Amended soil was then added to each cylinder
Figure 1. Experimental design for soil transport and photolysis experiments.
from the 3 cm depth to the top as before, with the weight of soil added to each cylinder recorded.

A second outdoor experiment was conducted to more closely approximate unsaturated flow conditions. In this case, the water table depth was kept at 15 cm below the soil surface for Callahan soil, or 25 cm for Montana soil. After adding the sterilized, clean soil with the water table at the 4.5 cm depth, the constant head tanks were lowered to the appropriate level prior to adding the amended soil. The water feeder hoses were filled with Callahan soil in order to maintain continuity with the water table. The soil surface was loosely covered by aluminum foil to avoid wind damage until the remainder of the soil bulk became wet via capillarity, which occurred in about 15 minutes for the 4.5 cm water depth, and in 1 to 2 hours for the 15 or 25 cm water table depth.

Five g control samples of amended soil were weighed into 40 mL amber tubes, and 1.2 g of distilled water were added to the Callahan soil samples, or 1.5 g to the Montana samples. The tubes were capped and covered with aluminum foil, and were placed in the field adjacent to the soil cylinders. The soils were irradiated in a fallow field at the Dept. of Environmental and Resource Sciences, University of Nevada, Reno.

**Soil Sampling.** The duplicate soil cylinders for each soil type and each treatment were sampled on days 2, 4 and 9 of the indoor experiment, and days 3, 7, and 14 of the outdoor experiments. The inflow hoses were clamped and
detached from the main feeder hoses to allow removal of the wet soils. The soil in each cylinder was then excavated cm by cm to the 4 cm depth into petri dishes. The soils for each layer were mixed thoroughly, and following mixing, two 5 g samples were weighed into 40 mL amber vials sealed with teflon septa for extraction, and the remainder of the soil layer was dried at 105 °C for soil moisture determination. Four control samples were also removed on each sampling day. All soil samples were stored in the dark at 4 °C until extracted.

**Extraction and Quantification.** Soil samples were extracted using 0.5 M NaOH in 30% methanol. Fifteen mL of the mixture were added to the soil in each tube, and the soils were then shaken in a horizontal position for 1 hour. After settling, the supernatant was decanted through Whatman 2V filter paper into a second 40 mL vial. The extraction was repeated using 10 mL of the extraction solution and shaking for 30 minutes. The entire sample and the empty vial were then rinsed into the filter paper using 70% methanol in water. When the soils had drained, 0.5 g of NaCl was added to the liquid, and the pH was adjusted to 2.0 using 1:1 v:v HCl:H₂PO₄. The sample was rinsed into a 125 mL separatory funnel using methanol, and the imazaquin was partitioned into 15 mL of methylene chloride three times. The combined methylene chloride layer was evaporated to dryness under nitrogen in a 38 °C water bath, and the residue was reconstituted in methanol. Recoveries from dry, unaged soil averaged
86.7% ± 2.6%. Average recoveries varied with moisture content and aging, with extractable residues decreasing somewhat with time.

Residues were quantified by HPLC as described above. Amounts present in the samples were determined from the standard curve constructed using the external standards. Detector response was linear within the range of concentrations used. The limit of detection was 5 ng/g of soil. Percent of imazaquin remaining in each soil layer was calculated on an air dry mass basis relative to the amount applied, and values were normalized by the average recovery from the control samples.

RESULTS AND DISCUSSION

Aqueous Photolysis Experiments. Plots of relative concentration vs. time were analyzed by least-squares regression to determine first order photolysis rate constants and half-lives. The half-life of imazaquin under the artificial lamps was 120 min, with a rate constant of 0.00576 min⁻¹ (R² = 0.989). No loss was observed in the aluminum foil-covered dark controls. Photolysis rates were faster in sunlight, with a half-life of 39 min in midday summer sunlight (Kp = 0.0178 min⁻¹; R² = 0.995). The clear plastic shield blocked the light slightly, and gave a longer half-life of 45 min when exposed at 20 cm below the plastic, or the level of the soil surface for the soil photolysis experiments (Kp = 0.0156...
min\(^{-1}\); \(R^2 = 0.997\)). Some photolysis did occur under the dark plastic, with a half-life of 950 min calculated (\(K_p = 0.00073\ \text{min}^{-1}; R^2 = 0.994\)).

These results suggest that rates of photolysis measured in the outdoor sunlight experiments under the clear plastic will be slightly slower than what would occur in full sunlight. A small amount of photodegradation can be expected in the dark controls due to incomplete shielding of the columns from sunlight.

**Batch Equilibrium Sorption Experiments.** Appreciable sorption of imazaquin on Callahan soil was not observed. Minimal sorption occurred on Montana soil, with a value of \(K_d\) of 0.1 mL/g calculated from a least squares linear regression as seen in Figure 2 (\(R^2 = 0.976\)). Goetz et al. (1986) measured sorption of imazaquin in five soils ranging from sandy loam to clay, and found sorption was minimal, with \(K_d\) values ranging from 0.001 (essentially unsorptive) to 0.21 mL/g in a fine sandy loam soil. Decreasing the pH resulted in increased sorption. This phenomenon was also reported by Loux et al. (1989b), who measured imazaquin adsorption on soils, sediments, and clays. Application of the Freundlich equation resulted in a statistical model for imazaquin adsorption which included soil pH, organic carbon, and clay as significant independent variables. Sorption was greater at pH values below 6 than at higher pH values. Similar results were reported by Che et al. (1992) who found that sorption of imazaquin increased as pH decreased, most notably from pH 5 to pH 3. Organic
Figure 2. Batch equilibrium sorption of imazaquin on Montana soil.
matter content appeared to be the major factor controlling sorption. Under acidic conditions, however, imazaquin molecules were protonated and sorbed to clay surfaces.

At most field pH values, imazaquin can be expected to be primarily anionic, with adsorption occurring via pH dependent charge generation in hydrous oxides and organic matter. At the pH of the soils used in these experiments, then, imazaquin should be present primarily in the soil solution, and thus should be highly mobile.

**Miscible-Displacement Experiments.** Similar results were found in the miscible-displacement experiments. Essentially no sorption occurred in either soil, as seen in Figure 3, with R values of 1 in Callahan soil (K_d = 0) and 1.034 in Montana soil (K_d = 0.02). The symmetrical shape of the data suggests that the process was essentially at equilibrium, although some irreversible sorption may occur over longer time periods, such as the 14 day scale of the outdoor soil photolysis experiments.

**Soil Transport and Photolysis Experiments.** Photolysis of imazaquin in Callahan soil subjected to near-saturated flow and irradiated with UV light was rapid, with 58% greater loss in the light-exposed soils than in the dark controls over the course of the experiment (Figure 4.) Some loss was seen from the dark controls, with 86.7% remaining at day 9. This may have been due to light scatter under the black plastic, or possibly due to some biodegradation occurring late in
Figure 3. Breakthrough curves for imazaquin on two soils
Figure 4. Irradiation of imazaquin on Callahan soil undergoing near-saturated flow and irradiated with UV light.

- ▽ = light, wet soils; ▼ = dark, wet soils;
- ■ = light, dry soils; □ = dark, dry soils.
the experiment. Only a small amount of loss was measured in the dry soils, with 7.5% less in the light-exposed dry soils than in the dark, dry controls. Recovery from these cylinders was greater than 100%, possibly due to actual recoveries from the soil which were higher than those measured in the aged control samples.

Some upward movement was seen in the air-dry soils, as shown in Figure 5, perhaps due to a small amount of evaporation which may have occurred due to warmer temperatures in the light bank, or due to minor volatilization. An average of 8.2% more imazaquin was present in the surface layer of the dark controls than in the light-exposed soils, suggesting that the primary mechanism of loss was photolysis, rather than volatilization.

Upward mobilization in the subirrigated columns, however, was rapid, with 85% of the initially applied mass found in the top 1 cm within 15 minutes after the soil surface became wet. Only 5% remained at the 2 to 3 cm depth. Imazaquin in the initially dry soil was partitioned into the soil solution almost immediately, and moved to the surface in a piston-flow like manner. This was expected given the lack of sorption measured in Callahan soil. Over time, however, increased concentrations were observed below the top 1 cm despite the average daily upward water flux of 1.8 cm/d in the light-exposed soils, and 2 cm/d in the dark controls, as shown in Figure 6. This may be due to a convective flux cell which
Figure 5. Distribution of imazaquin with depth in Callahan soil with no water added, and irradiation with UV light.
Figure 6. Distribution of imazaquin with depth in Callahan soil undergoing near-saturated flow and irradiated with UV light.
developed between the glass and the soil, resulting in downward movement, or perhaps is a consequence of downward diffusion.

The characteristic diffusion distance \( I_d \) is calculated as (Jury et al., 1984)

\[
I_d = \frac{D_E}{J_W}
\]

where \( J_W \) is evaporative flux and \( D_E \) is the effective soil diffusion coefficient, which is given in Jury et al. (1983) as

\[
D_E = \frac{D_{air} K_H a^{10/3} / \phi^2 + D_{water} \theta^{10/3} / \phi^2}{\rho_d K_d + \theta + aK_H}
\]

where \( D_{air} \) is the gaseous diffusion coefficient in air, \( D_{water} \) is the liquid diffusion coefficient in water, \( a \) is volumetric air content, and \( \phi \) is porosity. Given \( D_{air} = 0.43 \text{ m}^2/\text{d} \), \( D_{water} = 4.3 \times 10^{-5} \text{ m}^2/\text{d} \) (both from Jury et al., 1984), \( K_H = 2.87 \times 10^{-8} \) (dimensionless; calculated from solubility and vapor pressure data), \( a = 0.02 \), \( \theta = 0.4 \), and \( \phi = 0.42 \) (all from water retention function data for the soil), a characteristic diffusion distance of 0.16 cm can be calculated. Any downward movement of imazaquin will retard rates of photolysis in proportion to the amount of compound which is removed from the surface photic zone. With time, if downward diffusion results in redistribution with depth, rates of photolysis will become minimal unless upward transport continues.

Rates of loss were also rapid in Callahan soil exposed to sunlight when the water table was at the 4.5 or 15 cm depth. More loss was seen when the depth to water table was greater and unsaturated flow was occurring, with 58%
lost over 14 days as compared to 45% lost from the soils undergoing near-saturated flow (Figure 7). The variability between the replicate cylinders was also greater in the unsaturated flow outdoor experiment. While the amount of loss was similar to that observed in indoor, near-saturated flow experiment, despite slightly higher flux rates indoors, irradiation was limited to daylight hours. Overall rates of loss were thus greater in sunlight, as predicted by the aqueous photolysis data. Average daily flux was higher in the near-saturated flow outdoor experiment, and flux was lower in the dark controls due to decreased temperatures as a result of shading. Flux data are presented in Table 2.

Table 2. Average daily water flux in outdoor soil photolysis experiments.

<table>
<thead>
<tr>
<th>Flow Conditions</th>
<th>Depth to Water Table</th>
<th>Callahan Soil</th>
<th>Montana Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Light-exposed</td>
<td>Dark Controls</td>
<td>Light-exposed</td>
</tr>
<tr>
<td>near-saturated</td>
<td>4.5 cm</td>
<td>1.7</td>
<td>1.3</td>
</tr>
<tr>
<td>unsaturated</td>
<td>15 or 25 cm</td>
<td>0.84</td>
<td>0.76</td>
</tr>
</tbody>
</table>

The greatest distinction between the two outdoor experiments is the difference in amounts of downward movement of imazaquin. By day 14, very little imazaquin was present below the top 1 cm in the unsaturated flow experiment, but up to 11.4% was found below 3 cm in one dark treatment in the near-saturated flow experiment, as shown in Figures 8 and 9. The difference in
Figure 7. Irradiation of imazaquin on Callahan soil undergoing (a) near-saturated and (b) unsaturated flow.

- □ = light-exposed; • = dark controls.
Figure 8. Distribution of imazaquin with depth in Callahan soil undergoing near-saturated flow and irradiated with sunlight.
Figure 9. Distribution of imazaquin with depth in Callahan soil undergoing unsaturated flow and irradiated with sunlight.
behavior suggests that diffusion was occurring over greater distances in soils which were wetter; or alternatively, in saturated soils, a convection cell may have developed along the surface of the glass cylinder. A gradient of less than 3% in soil moisture by weight was measured in the experiment with the water table at 4.5 cm, with the surface soils nearing saturation. In the unsaturated flow experiment, a gradient of up to 9% was observed, with visibly dryer soil at the surface. The dryer soil is not expected to maintain a convective flow along cell walls, thus decreasing downward movement.

The equation used above to estimate characteristic diffusion distances suggests that the amount of diffusion will be maximized when $\theta$ is greatest. Using values from soil moisture retention data of $a = 0.05$, $\theta = 0.37$, and $t = 14$ days for the unsaturated flow experiment, a lower value of $D_E$ of $2.4 \times 10^{-5} \text{ m}^2/\text{d}$ results in a characteristic diffusion distance of 0.29 cm, as compared to 0.19 cm for the near-saturated flow experiment ($D_E = 2.87 \times 10^{-5} \text{ m}^2/\text{d}$). The larger value calculated for the unsaturated flow experiment is due to the decrease in evaporative flux.

The values presented do not appear to explain the lack of downward migration in the dryer soils. However, as soil moisture decreases, sorption generally increases, with a maximum in dry soils. If the surface 1 mm was sufficiently dry, imazaquin would tend to be retained in this zone. Goetz et al. (1986) found that temporary drying of soils to 25 to 50% of field capacity resulted
in maximum sorption of imazaquin. At lower water contents, imazaquin is drawn closer to the soil surfaces, which may increase the amount of sorption. Thermal gradients in the soil were similar during both experiments, suggesting that this is not an important mechanism for downward movement of imazaquin. The lack of downward migration may be due to the absence of downward transport along the glass cylinder walls in these dryer soils.

Photolysis of imazaquin in Montana soil was slower, with 31% lost in the near-saturated flow experiment after 14 days, and 29% in the unsaturated flow experiment, as compared to dark control soils (Figure 10). Recovery from the dark controls was low, with less than 80% remaining at the end of both experiments. The reason for this loss is unclear, but it may be related to biodegradation or inextractable residues which increased as the soils aged.

A similar difference in the depth profiles was also seen, with more present with depth in the near-saturated flow experiment than in the unsaturated flow experiment on day 7, although little imazaquin remained below the top cm by day 14 except in the dark controls in the near-saturated flow experiment (Figures 11 and 12). Data from the day 3 dark controls in the unsaturated flow experiment is missing due to equipment failure.
Figure 10. Irradiation of imazaquin on Montana soil undergoing (a) near-saturated and (b) unsaturated flow. □ = light-exposed; • = dark controls.
Figure 11. Distribution of imazaquin with depth in Montana soil undergoing near-saturated flow and irradiated with sunlight.
Figure 12. Distribution of imazaquin with depth in Montana soil undergoing unsaturated flow and irradiated with sunlight.
Estimates of distances of downward diffusion are only slightly lower than for the Callahan soil due to slight sorption in this soil, with estimates of 0.18 and 0.25 cm, respectively, for the near-saturated and unsaturated flow conditions when $t = 14$ days. These values were calculated using data from Table 3.

Table 3. Soil parameters used in estimating diffusion in Montana soil.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Depth to water table, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil bulk density, $\rho_b$, kg/m$^3$</td>
<td>4.5 cm: 1050</td>
</tr>
<tr>
<td>Volumetric water content, $\theta$, m$^3$/m$^3$</td>
<td>0.60</td>
</tr>
<tr>
<td>Volumetric air content, $\alpha$, m$^3$/m$^3$</td>
<td>0.04</td>
</tr>
<tr>
<td>Porosity, $\phi$, m$^3$/m$^3$</td>
<td>0.64</td>
</tr>
<tr>
<td>Sorption coefficient, $K_d$, m$^3$/kg</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

Differences in rates of photolysis of imazaquin between the two soils can be attributed both to differences in rates of convective transport and diffusion, and to differences in the character of the soil surface. Variations in color, pore sizes, particle sizes, sorption, and presence of quenchers will all result in different rates of photolysis on soil surfaces (Miller and Donaldson, 1994). Successful modeling of photolysis in soils will thus depend both on transport characteristics of the matrix and the individual chemical, and upon surface properties which will affect photolysis rates.

These experiments have demonstrated that transport of imazaquin upward with evaporating water can substantially increase rates of
photodegradation in soils. This information is useful in planning type and rate of field application, timing of irrigation, and in estimating future year residues. The potential for remediation of contaminated areas also exists where an artificial, shallow water table can be maintained. Residues will be highest in low pH soils which are moderately sorptive, and where cool, moist conditions decrease rates of evaporation.

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Chapter 4.

Transport and Photolysis of Pentachlorophenol in Soils
ABSTRACT

Pentachlorophenol (PCP) was applied to loamy sand and sandy clay loam soils to determine the effect of upward evaporative flux on rates of transport and photolysis. Subirrigated soil columns were irradiated by ultraviolet lamps or sunlight to measure relative rates of photolysis under differing soil moisture regimes. Photolysis was initially rapid in loamy sand soil under near-saturated flow conditions, with up to 55% lost in light-exposed treatments in 14 days as compared to dark controls. Rates of transport were slower in sandy clay loam soil, reflecting a soil sorption distribution coefficient of 10 mL/g, as compared to 0.4 mL/g in the loamy sand. Despite slower upward movement, similar amounts of photodegradation of PCP had occurred in the sandy clay loam soil after 14 days. Dropping the water table to the 15 cm depth resulted in unsaturated flow and increased losses to volatilization, with a much lower relative contribution of photodegradation over the course of the experiments. Up to 77% was lost from the loamy sand soil dark treatments during the 14 day period. The volatile product was trapped in a closed system using $^{14}$C-PCP, and was identified as the parent molecule. Processes which translocate PCP into the sunlit surface zone under near-saturated soil moisture conditions can be expected to enhance rates of photolysis while minimizing volatilization.
INTRODUCTION

Pentachlorophenol (PCP) has been used worldwide for over 50 years as a general biocide (Bevenue and Beckman, 1967; Boyd et al., 1989). Its major application today is in the treatment and preservation of wood products (Kitunen et al., 1987). In the past, PCP was used in many agricultural applications, notably in rice fields in Japan. It has been detected in air in pristine areas, as well as in groundwater and surface water, with concentrations in the mg L⁻¹ range near some industrial discharges (Wild et al., 1992). Soil contamination of up to 658 mg/kg was measured adjacent to poles treated with PCP (WHO, 1987), with even greater concentrations present in soils at preserving facilities (Valo et al., 1984; Kitunen et al., 1987).

Since PCP is toxic to most life forms, understanding its fate in the environment is necessary for safe use and management. Once released, PCP is subject to volatilization, adsorption, leaching and degradation by both biological and nonbiological means. Volatilization can be an important source of loss of PCP from water and soil surfaces, as well as from treated materials (WHO, 1987). Adsorption in soils appears to be controlled by pH, with sorption at a maximum in strongly acidic soils, and much lower in neutral soils (Boyd et al., 1989). With a \( pK_a \) of 4.75, the solubility and rate of leaching of PCP increases with increasing pH; at pH 5, the solubility of PCP is 14 to 19 mg L⁻¹ (20 °C) while at pH 8, the solubility is 8000 mg L⁻¹ (WHO, 1987; Lee et al., 1990).
Soil organic matter content and surface area also influence sorption and leaching behavior.

Biodegradation of PCP may occur via aerobic and anaerobic processes, although high concentrations are probably inhibitory to indigenous microorganisms (Boyd et al., 1989). Half-lives from a few weeks to >1 year have been measured (Bajpai and Banerji, 1992).

Photochemical transformation of PCP in water and soil occurs readily via a number of pathways (Goshal et al., 1992; Wong and Crosby, 1981; Hwang et al., 1986). Rates are more rapid at neutral pH, and can be accelerated if catalyzed by semiconductors such as zinc and titanium dioxide (WHO, 1987). Goshal et al. (1992) found that approximately 40% of PCP applied to thin soil films was lost after irradiation in a photoreactor, with less than 5% loss in dark controls. Photolysis rates are dependent on light available for initiating reactions, and attenuation of light by natural chromophores is known to decrease rates of photolysis, both in water (Pignatello et al., 1983; Hwang et al., 1986) and also in soils, where the depth of light penetration is limited to the top 0.5 mm of soil (Hebert and Miller, 1990).

Using thin soil films to measure rates of soil photolysis neglects processes which may transport the chemical into the photic zone. If PCP is dissolved in the soil solution and can be transported upward with evaporating water, rates of photolysis are expected to increase as a function of the amount of time PCP is
present at the soil surface. The objectives of this research are (i) to determine the rate of photolysis of PCP in soils undergoing an evaporative flux and (ii) to relate these rates to processes affecting transport of PCP in soils.

**MATERIALS AND METHODS**

Pentachlorophenol (>99% pure) and diazald (99%) were purchased from Aldrich. Purity of PCP was verified by high performance liquid chromatography (HPLC) using a Supelco DB-8-LC column with an acetonitrile-water mobile phase acidified to pH 3 with acetic acid, and a Linear 200 UVIS detector set at 304 nm. Pentachlorophenol-\(^{14}\)C (2.65 mCi mmol\(^{-1}\)) was obtained from Sigma Chemical Co. High purity solvents, buffers and reagents were obtained from Fisher Scientific. Sep-Pak C\(_{18}\) cartridges were obtained from Millipore Corp., and Hepa-Vent 0.3 \(\mu\)m in-line glass microfiber filters were purchased from Whatman. All water used in these experiments was buffered to pH 7 using 16 mM sodium phosphate dibasic and potassium phosphate monobasic.

Stock solutions of PCP were prepared in toluene to 4 mg mL\(^{-1}\), and were further diluted with toluene to give a range of standards from 0.008 to 1.6 \(\mu\)g mL\(^{-1}\). Standards were derivatized using diazomethane distilled from an ether solution of Diazald. Stock and standards were stored at 4 °C in amber glass vials sealed with teflon-coated septa.
The soils used for this study were a loamy sand collected from the 0 to 50 cm depth increment at a range site in Washoe County, Nevada ("Callahan"), and a sandy clay loam collected from the 0 to 30 cm depth increment 25 miles south of Plentywood, in Sheridan County, Montana ("Montana"). Callahan consisted of 82% sand, 10% silt and 8% clay, with a soil-solution pH of 7.3, a cation exchange capacity (CEC) of 4 mequiv 100 g⁻¹ and 0.3% organic matter. Montana contained 48% sand, 24% silt and 28% clay, with a soil-solution pH of 7.9, a CEC of 10 mequiv 100 g⁻¹ and 1.7% organic matter. The soils were air-dried and passed through a 1-mm sieve prior to autoclaving to ensure initial sterility.

**Batch Equilibrium Sorption Experiments.**

Isotherms for PCP were measured for each soil using the batch equilibration method (Rao et al., 1990). Four grams of soil were placed in 15 mL test tubes, and ten mL of various concentrations (0.008, 0.016, 0.08, 0.24, 0.8, and 1.6 μg mL⁻¹) of PCP dissolved in pH 7 buffer were added to the soil. The tubes were closed with polypropylene screw caps and shaken in a horizontal position for 24 hours at room temperature (T = 24 °C ± 1 °C). This time period was previously found to be sufficient for equilibration to occur, without measurable degradation (Lee et al., 1990). Four replications were made at each concentration for each soil, and solvent and soil blanks were included at each concentration to rule out decomposition.
Following equilibration, the tubes were centrifuged and 3 mL of supernatant were withdrawn. Three mL of toluene was added to each sample, including the original stock solution for each concentration, and the tubes were shaken for 30 minutes to allow partitioning. PCP in aliquots of the toluene layer was derivatized as before. Samples were analyzed by gas chromatography with electron capture detection (GC-ECD), using nitrogen as the carrier gas. The column used was a 15 m x 0.53 mm i.d. Supelco SPB-5 with a 1.5 μm film thickness. The oven was maintained at 180 °C, and the retention time was 5.7 minutes with a column flow rate of 6 mL min⁻¹.

Sorption coefficients, \( K_d \) (mL/g) were determined by fitting a linear model to the sorption data, such that \( S = K_d C \), where \( S \) and \( C \) are the sorbed (μg g⁻¹ soil) and solution concentrations (μg mL⁻¹), respectively, at equilibrium. That fraction of PCP which had been removed from the solution was assumed to be sorbed onto the soil.

**Aqueous Photolysis**

Rates of aqueous photolysis for PCP were determined in midday sunlight at the beginning and end of each soil photolysis experiment. Stock solution was diluted in pH 7 buffer to \( 3 \times 10^{-4} \) M and placed in 25 mL borosilicate glass test tubes with teflon-lined caps, with two replicates for each treatment. The tubes were placed in full sun, under clear, polyethylene plastic, and under black plastic, and were sampled at intervals of 15, 30, 60 and 120 minutes. Samples
were placed directly in amber autosampler vials and stored at 4 °C until analyzed.

Rates of aqueous photolysis were determined in a similar manner under ultraviolet (UV) light using a bank of 16 Westinghouse FS40 lamps (λ\textsubscript{max} = 310 nm). Dark controls were covered with aluminum foil. The tubes were placed 30 cm below the lamps, and temperatures were maintained at 30 °C ± 2 °C.

Residues were quantified by HPLC using a Hewlett Packard 1050 Liquid Chromatograph coupled to a Linear 200 UVIS Detector set at 304 nm. A Hewlett Packard 3396A integrator was used for quantitation. The HPLC was operated isocratically at 1.25 mL min\textsuperscript{-1} using 50% acetonitrile and 50% water with 1% acetic acid as the mobile phase. The column used was a 15 cm long reversed phase Supelco DB-8-LC with 4.6 mm i.d. x 5 µm packing material. Under these conditions, the retention time was 5.2 minutes. First-order photochemical rate constants were determined using the integrated expression for first order reactions.

**Soil Transport and Photolysis Experiments.**

Four soil photolysis experiments were conducted to determine the effect of upward transport on rates of photolysis. Two experiments were conducted under near-saturated flow conditions, with the depth to water table at 4.5 cm. Callahan soil containing 1.5 µg g\textsuperscript{-1} PCP was irradiated indoors using the bank of 16 UV lamps (started 4/1/92). Treatments included light-exposed or light-
shielded soils undergoing constant evaporation with near-saturated flow conditions; and light-exposed or light-shielded air dry soils receiving no water. A second near-saturated flow experiment with the water table at 4.5 cm was started 8/17/92 in which both soils were irradiated simultaneously in sunlight.

A third experiment started 8/2/93 was performed outdoors in sunlight using both soils containing 1.5 μg g⁻¹ PCP, but with the depth to water table at 15 cm below the soil surface to ensure unsaturated flow was occurring over the column length. A final radiolabeled experiment was begun 11/9/93 using the UV lamps to irradiate ^14C PCP in Callahan soil in a closed system with upward evaporation from a water table at the 15 cm depth.

Rotary evaporation under a vacuum was used to amend the soils to 1.5 μg g⁻¹ PCP, or 6 μg g⁻¹ ^14C PCP (60 nCi g⁻¹), with methylene chloride as the solvent. Concentrations in the soil were homogeneous, and were verified by extracting and quantifying a series of soil samples.

For the indoor near-saturated flow experiment, cylinders 5.5 cm i.d. x 5.5 cm in length were constructed from glass tubing, with open tops and closed bottoms fitted with 0.5 cm glass tubing to allow water inflow from the bottom of the cylinder. Buffered distilled water was supplied to the cylinders via Tygon tubing attached to individual water reservoirs, which were covered with parafilm and aluminum foil to avoid evaporative loss. Reservoirs were filled daily to
measure water consumption. Variability measured in the individual reservoirs was within ±5%.

At the start of the experiment, replicate cylinders (two per treatment per sampling day) were placed in foam insulated boxes in the light bank. The water level in the cylinders was adjusted to the 4.5 cm depth, the inflow tube was covered by glass wool, and unamended sterilized soil was placed atop the glass wool to a depth of 3 cm in each cylinder. Wetting of the soil was rapid. Once the soil was wet, a measured amount of amended soil containing POP was placed atop the wetted soil. The water level in the reservoirs was maintained at the 4.5 cm depth in the soil at all times. Two control cylinders were filled in the same manner, but the hoses were clamped and the soil sampled 15 minutes after the soil surface was visibly wet. This allowed determination of initial distribution of PCP with depth at the beginning of the experiment.

At the same time, four cylinders with sealed bottoms were filled with dry sterilized soil to the 3 cm depth, and amended soil to the surface. These cylinders received no water throughout the experiment, and were used to measure photodegradation in air-dry soil. Control samples (3 g amended soil plus enough water to saturate, plus 3 g dry samples) were also weighed into test tubes covered with aluminum foil, sealed, and placed in the light bank to monitor extraction efficiency over the course of the experiment.
Soils which were to be irradiated were placed 30 cm below the FS40 lamps used for the aqueous photolysis experiments. Dark controls were shielded from light by placing black plastic 10 cm above the soil surface. This allowed evaporation to occur in the absence of light. Constant air flow across the soils was maintained by a series of fans, and temperatures were 30 °C ± 2 °C. The soils were irradiated constantly for 9 days. Light intensity averaged 115 μwatts cm⁻² at the soil surface for the light-exposed treatments, and 3 μwatts cm⁻² at the surface of the dark controls.

The design of the near-saturated flow outdoor experiment was similar, with the same glass cylinders used, but both soils were irradiated simultaneously. The six cylinders for each treatment in each soil type were supplied with buffered distilled water from a single constant head tank, which was maintained by a 2 L Erlenmeyer flask. The four water tanks and their Erlenmeyer flasks were covered with tarpaulins to minimize temperature fluctuations. Daily measurements of water consumption were made by refilling the flasks.

At the start of each outdoor experiment, replicate cylinders (two per treatment per soil per sampling day) were placed in foam insulated boxes 20 cm below the clear and black plastic shields, as seen in Figure 1. For the first outdoor experiment, the water table was maintained at the 4.5 cm depth in the soil, allowing near-saturated flow to occur. Amended soil was then added to
Figure 1. Experimental design for soil transport and photolysis experiments.
each cylinder from the 3 cm depth to the top as before, with the weight of soil added to each cylinder recorded.

In the second outdoor experiment, the water table depth was kept at 15 cm below the soil surface for Callahan soil, or 25 cm for Montana soil, resulting in unsaturated flow. After adding the sterilized, clean soil with the water table at the 4.5 cm depth, the constant head tanks were lowered to the appropriate level prior to adding the amended soil. The water feeder hoses were filled with 1 mm grain size sand in order to maintain continuity with the water table. The soil surface was loosely covered by aluminum foil to avoid wind damage until the remainder of the soil bulk became wet via capillarity, which occurred in about 15 minutes for the 4.5 cm water depth, and in 1 to 2 hours for the 15 or 25 cm water table depth.

Three g control samples of amended soil were weighed into test tubes, and 0.8 g of distilled water were added to the Callahan soil samples, or 1.2 g to the Montana samples. The tubes were capped and covered with aluminum foil, and were placed in the field adjacent to the soil cylinders. The soils were irradiated for a two week period in a fallow field at the Dept. of Environmental and Resource Sciences, University of Nevada, Reno.

The design for the indoor radiolabeled experiment was similar to that of the first indoor experiment, with the exception that the water table depth was maintained at the 15 cm depth. Only Callahan soil was used. Two light-exposed
and two dark controls were irradiated for a period of 14 days using the UV lamps. A single initial cylinder was also prepared and sampled 15 minutes after the soil surface had wetted as before.

For this experiment, special cylinders were constructed which had two air inflow tubes placed 1 cm below the top of the cylinder, and a single air outflow tube at the same depth. The cylinders were fed with buffered water from below, as before, with individual constant head tanks used for each cylinder. The water supply tubes were again filled with clean 1 mm sand. The cylinders were filled with clean, sterilized soil to within 3 cm below the air tubes, and amended soil to the bottom of the air tubes (soil surface level). After the soils had wet to the surface, polyethylene film was used to seal the cylinder tops, and the dark treatments were also covered with black plastic to totally exclude light. A 2 cm deep air space was left between the plastic film and the soil surface, for an air space volume of 47.5 cm$^3$. The air intake tubes for each cylinder were connected to Hepa-Vent 0.3 μm glass microfiber filters to sterilize incoming air. Connected in parallel to the air outflow tube were two Sep-Pak C$_{18}$ sorbent cartridges to capture volatile products, then two 1 M ethanolamine CO$_2$ traps, and an empty flask to capture base and water condensation. All four soil cylinders were connected to a single vacuum pump to provide constant air flow across the soil surface during the 14 day irradiation period. Aluminum foil
covered controls consisting of 4 g soil plus 1 g buffer were placed alongside the soils in the light bank.

**Sampling, Extraction and Quantification**

The duplicate soil cylinders for each soil type and each treatment were sampled on days 0, 2, 4 and 9 of the indoor near-saturated flow experiment, days 3, 7, and 14 of the outdoor experiments, and days 0 and 14 of the unsaturated flow radiolabeled experiment. The inflow hoses were clamped and detached from the main feeder hoses to allow removal of the wet soils. The soil in each cylinder was then excavated cm by cm to the 4 cm depth into petri dishes. The soils from each layer were mixed thoroughly, and following mixing, two 4 g samples were weighed into test tubes for extraction. The remainder of the soil layer was dried at 105 °C for soil moisture determination. Four control samples were also removed on each sampling day, and all soil samples were stored in the dark at 4 °C until extracted.

Soils containing 14C PCP were sampled in the same manner through the entire 5 cm soil depth, with 6 g samples retained for extraction. The Sep-Pak cartridges were eluted with 3 to 6 mL of methanol nine times and the polyethylene film was retained for direct scintillation counting.

PCP was extracted from the soils using 0.5 m KOH after the method of Stark (1969). Following extraction with base, the solution pH was adjusted to between 6.5 and 7 using 6N H₂SO₄, and the PCP was partitioned into toluene.
Aliquots of the toluene extract were derivatized as before. Recoveries from dry, unaged soil averaged 91 ± 3%. Recoveries from Callahan soil did not vary greatly in the wet, aged controls, but inextractable residues increased in Montana soil over time, presumably due to irreversible sorption.

Residues of unlabeled PCP were quantified by GC-ECD as described above. Amounts present in the samples were determined from a standard curve constructed using external standards. Detector response was linear within the range of concentrations used, and the limit of detection was 50 pg g⁻¹ of soil. Percent of PCP remaining in each soil layer was calculated on an air-dry mass basis relative to the amount applied, and values were normalized by the average recovery from the control samples.

Radiolabeled PCP was quantified using a Beckman LS 1701 Liquid Scintillation counter (¹⁴C efficiency = 96%). Samples of the toluene extract, the methanol trap extract, and the base in the traps and water collected in the flasks were counted in Ecodeum scintillation cocktail. The polyethylene film was placed in 20 mL scintillation vials, cocktail was added, and residues were counted directly. A Radiomatic detector coupled to an HPLC was used to verify compound identity in the extract from the Sep-Pak traps. Thin layer chromatography (TLC) of the soil extract was accomplished using silica gel plates which were developed in 100:25:2:2 methylene chloride:1-propanol:formic
acid: distilled water. The plates were read using a Bioscan System 200 Imaging Scanner.

**RESULTS AND DISCUSSION**

**Batch Equilibrium Sorption**

Sorption of PCP was much greater on Montana soil, with a value of $K_d$ calculated as 10 mL g$^{-1}$ ($R^2 = 0.994$) as compared to a $K_d$ of 0.4 mL g$^{-1}$ ($R^2 = 0.988$) measured for Callahan soil. The linear model provided an adequate fit for this range of concentrations (Figure 2).

The values measured are within the range of $K_d$ values seen in other soils. Lee et al. (1990) measured $K_d$ in soils at near-neutral pH values with organic carbon contents varying from 0.22 to 3.4% and found values of $K_d$ which ranged from 0.64 to 28.1 when the ionic strength was 0.015 or lower. As ionic strength increased, distribution coefficients increased by a factor of about 6. The higher salt concentrations appear to favor the formation of ion pairs (Westall et al., 1985), or to alter the exchangeable cations on the soil surface. Some sorption of the anion may also occur, with the relative contribution of sorption of the ionized PCP to the total being a function of pH and ionic strength, as well as the organic carbon content of the sorbent (Schellenberg, et al., 1984). The greater amount of organic matter in Montana soil is likely responsible for the increase in sorption noted.
Figure 2. Batch equilibrium sorption of pentachlorophenol on two soils.
The retardation factor, R, which is an index of the mobility of a solute being eluted through a soil column, can be calculated as

\[ R = 1 + \frac{\rho_b K_d}{\theta} \]

where \( \rho_b \) is soil bulk density and \( \theta \) is volumetric water content (Nkedi-Kizza et al., 1987). For Callahan soil, given \( \rho_b = 1.45 \text{ g cm}^{-3} \) and \( \theta = 0.4 \) or 0.37 (from water retention function data), \( R_L \) can be estimated as 2.45 when the water table is at 4.5 cm, and 2.57 at the 15 cm depth. Far more retardation is expected in Montana soil due to more sorption, with values of 18.3 and 20.4 calculated, respectively, given \( \rho_b = 1.05 \text{ g cm}^{-3} \) and \( \theta = 0.6 \) or 0.54. This suggests that PCP should reach the soil surface rapidly in Callahan soil, and much more slowly in Montana soil.

**Aqueous Photolysis**

Photolysis of PCP was first order with respect to concentration. The half-life under the UV lamps was 125 minutes, with a rate constant \( K_p \) of \( 5.55 \times 10^{-3} \text{ min}^{-1} \) (\( R^2 = 0.999 \)). Rates of photolysis were more rapid in sunlight, with a half-life of 24 minutes in full sunlight (\( K_p = 2.88 \times 10^{-2} \text{ min}^{-1}; R^2 = 0.989 \)); 30.9 under the clear plastic (\( K_p = 2.24 \times 10^{-2} \text{ min}^{-1}; R^2 = 0.987 \)); and 635 minutes under the black plastic (\( K_p = 1.09 \times 10^{-3} \text{ min}^{-1}; R^2 = 0.994 \)). The slower rates of photolysis under the clear plastic suggest that rates of photolysis measured in the outdoor soil experiments are conservative.
These results for direct photolysis of ionized PCP are generally consistent with those of Hwang et al. (1986), who measured rates of photolysis of chlorophenols in surface estuarine water and found a half-life of 180 min for PCP in December, with faster rates in summer sunlight. In distilled water at pH 7.7 in summer sunlight, a half-life of 1 h was measured. At near neutral pH values, then, aqueous photolysis rates will be rapid.

**Soil Photolysis Experiments**

*Near-saturated flow experiments*

Initial loss of PCP in Callahan soil during the first four days in the laboratory irradiated near saturated flow experiment was rapid, with 28% more lost in the light treatments as compared to the dark controls, as can be seen in Figure 3. Little additional loss due to photolysis was seen, with only 3% more degraded by day 9. A substantial amount of PCP was lost from the dark controls, with up to 46% missing from one cylinder on day 9. While the rate of upward movement in the initial cylinder was relatively slow, with up to 22% remaining in the third cm and up to 41% in the second cm, upward movement of PCP continued, with a maximum of 17% left below the top 1 cm on day 2.

The measured average daily flux, \( J_w \), of 1.7 cm d\(^{-1} \) can be used to estimate a relative time \( t_c \) to reach a distance \( l \) in solution as \( t_c = l / V_E \), where

\[
V_E = J_w / ( \rho_b K_d + \theta + a K_H )
\]
Figure 3. Irradiation of pentachlorophenol on Callahan soil under near-saturated flow conditions in UV light.

= light, wet soils; = dark, wet soils;
= light, dry soils; = dark, dry soils.
where $a$ is the volumetric water content and $K_H$ is Henry's constant (Jury et al., 1984). Given a value of $K_H$ of $1.15 \times 10^{-4}$ (dimensionless) calculated from solubility and vapor pressure data at 20 °C, and a value of $a$ of 0.02, travel time to reach the soil surface is estimated as 1.73 days.

By day 9, however, some downward redistribution had occurred, with up to 5.6% in the fourth cm in one dark treatment (Figure 4). This may be due to downward diffusion in the liquid solution. The characteristic diffusion distance can be estimated as

$$d = \frac{D_{E}}{J_{W}}$$

where the effective diffusion coefficient, $D_{E}$, can be estimated as

$$D_{E} = \frac{D_{air}^{\text{eff}} K_H a^{10/3} / \phi^2 + D_{water}^{\text{water}} \theta^{10/3} / \phi^2}{\rho \phi K_d + \theta + a K_H}.$$

where $J_W$ is the evaporative water flux, $D_{air}^{\text{eff}}$ is the gaseous diffusion coefficient in air ($4.3 \times 10^{-1}$ m$^2$ d$^{-1}$), $D_{water}^{\text{water}}$ is the liquid diffusion coefficient in water ($4.3 \times 10^{-5}$ m$^2$ d$^{-1}$), and $\phi$ is porosity (0.42). Estimates of $D_{E} = 1.17 \times 10^{-5}$ and $l_d = .078$ cm can be calculated. Diffusion thus may account for some minor redistribution of PCP during the experiment. Volatile travel in the soil bulk should be minimal, due to the near saturated conditions in the soil and the small amount of air-filled porosity.

Little loss or movement of PCP was seen in the dry soils, with 6% less in the light treatments by day 9 (Figure 5). Recovery in the dark controls averaged
Figure 4. Distribution of pentachlorophenol with depth in Callahan soil under near-saturated flow conditions and irradiation with UV light.
Figure 5. Distribution of pentachlorophenol with depth in Callahan soil with no water added, and irradiation with UV light.
96%. If photolysis depths are limited to the top 1 mm of the soil bulk, 3.3% would be expected to be lost. Some upward movement of PCP may have occurred to account for the slightly greater amount of loss seen in the dry soils.

Under outdoor near-saturated flow conditions with the water table at 4.5 cm, more loss was observed in Callahan soil, with 55% more lost in the light exposed soils as compared to the dark controls (Figure 6). Up to 42% was lost in one dark treatment by day 14. The more rapid rate of photolysis parallels the more rapid rate of aqueous photolysis measured in sunlight. Some downward redistribution was again noted, with up to 3.7% in the fourth cm in one dark treatment, as seen in Figure 7.

The average daily flux was 1.6 cm d⁻¹ in the light-exposed soils, and 1.2 cm d⁻¹ in the dark controls, with the lower rate of evaporation in the darks due to physical shading and cooling of the soil surface. Travel times are thus somewhat less than in the indoor near-saturated flow experiment, with estimates of 2 and 2.3 days to reach the soil surface in the light-exposed and dark soils.

The pattern of loss in the outdoor near-saturated flow experiment in Montana soil was quite different, reflecting the 7 to 8 times greater retardation expected in this soil. As seen in Figure 6, the initial rate of loss was relatively slow, with 21% lost over the first 3 days. Flux rates of 1.6 cm d⁻¹ in the light-exposed soils and 1.25 cm d⁻¹ in the dark controls were similar to those for Callahan soil, reflecting the shallow water table depth. By day 14, however,
Figure 6. Irradiation of pentachlorophenol in near-saturated flow conditions in (a) Callahan and (b) Montana soils. □ = light-exposed; • = dark controls.
Figure 7. Distribution of pentachlorophenol with depth in Callahan soil under near-saturated flow conditions and irradiation with sunlight.
more loss was measured than in Callahan soil, with an average of 58% greater loss in light exposed soils than in the dark controls. Upward transport was indeed slower in Montana soil, but less downward redistribution occurred by day 14 (Figure 8). Relative estimates of travel time of 22.2 and 26.4 days to reach the soil surface in the light-exposed and dark soils would appear to exceed actual rates of transport. The calculated characteristic diffusion distance was .012 cm.

**Unsaturated flow experiments**

When the water table was lowered to the 15 cm depth, rapid initial photolysis of pentachlorophenol in Callahan soil was noted on day 3 of the outdoor experiment, with an average of 40% lost. With increasing time, however, more was lost from the dark controls than from the light-exposed soils, with only 17% difference on day 14, as can be seen in Figure 9. Less downward redistribution was noted in this experiment (Figure 10). Rates of flux were lower, with an average of 1.25 cm d
\(^{-1}\) in the light-exposed soils, and 0.88 cm d
\(^{-1}\) in the dark controls. Liquid solution travel times are thus expected to be somewhat slower, or 2.3 and 3.2 days, respectively, to reach the soil surface. Liquid diffusion decreases as a function of \(\theta\) (0.37), for an estimated distance of .074 cm.

As the fraction of air-filled pores increases, the rate of volatilization is also expected to increase. As PCP was relocated to the soil surface over time,
Figure 8. Distribution of pentachlorophenol with depth in Montana soil under near-saturated flow conditions and irradiation with sunlight.
Figure 9. Irradiation of pentachlorophenol in unsaturated flow conditions in (a) Callahan and (b) Montana soils. □ = light-exposed; • = dark controls.
Figure 10. Distribution of pentachlorophenol with depth in Callahan soil under unsaturated flow conditions and irradiation with sunlight.
increasing amounts of volatilization may have occurred as a consequence of increasing soil solution concentrations due to decreasing soil moisture content. It is also possible that biodegradation contributed to some of the loss seen by day 14, although lag periods are generally longer when the soil has not been previously exposed to PCP.

When the water table was lowered to 15 cm in Montana soil in the outdoor experiment, once again loss from the dark controls was substantial. The difference between the light and dark treatments decreases slightly with time, with an average of 16.8% less in the light-exposed soils on day 14 (Figure 9). Average daily flux was greater than that measured in Callahan soil undergoing unsaturated flow, at 1.4 and 1.1 cm d\(^{-1}\), respectively, in light-exposed and dark soils. The rate of loss was again slower than that seen in Callahan soil. This corresponds to slower estimated rates of upward transport (23 and 29 days), with as much as 20% still present in the third cm on day 3 (Figure 11). The estimated characteristic diffusion distance decreased to 0.0085 cm.

**Radiolabeled tracer experiment**

The radiolabeled experiment was undertaken in order to determine the relative rates of volatilization and photolysis in Callahan soil subjected to unsaturated flow conditions. Recovery in the initial cylinder was 100.7%, with 47% present in the top 1 cm, 42.2% in the next cm, and only trace amounts present below the 3 cm depth. By day 14, 32.2% and 50.4% was present in the
Figure 11. Distribution of pentachlorophenol with depth in Montana soil under unsaturated flow conditions and irradiation with sunlight.
top cm of the light-exposed soils and dark controls, respectively, as an extractable form of PCP, with less than 10% remaining below the top cm. No photoproducts were seen on TLC of the extract, with only PCP identified. Three percent was recovered from the base and water traps in the light-exposed treatments, with only 0.17% recovered in the dark controls. The difference can be attributed to complete mineralization of PCP via photolysis.

Volatile PCP was trapped in both treatments, with 9% and 11.7% from the light-exposed and dark controls, respectively. The identity of the volatile material was confirmed using HPLC retention times and relative amounts present in scintillation counting as compared to integrated peak areas. Only a single peak was noted, which was identified as the parent compound, and >96% of the volatile radioactivity in the sample was accounted for. While PCP is very soluble in the phenolate form at pH 7, and thus might be expected to remain in the soil solution, there is evidence to suggest that increased acidity in the microenvironment around soil particles may influence the sorption and volatilization of PCP in soil (Schwarzenbach et al., 1993). To support this theory, only minor amounts of volatilization have been measured from water (Pignatello et al., 1983; Goshal et al., 1992).

Volatilization of soil-incorporated pesticides is a function of the vapor pressure of the chemical at the soil surface, which is modified by adsorption, and the rate of movement to the soil surface by diffusion or convection with
evaporating water. The smaller amount of volatile loss in the radiolabeled experiment than was seen in the outdoor experiments may be a function of rates of evaporative flux. Due to the relatively high humidity in the boundary layer in the radiolabeled experiment, evaporative flux averaged 0.5 cm d$^{-1}$, as compared to 1.25 cm d$^{-1}$ for similar conditions in outdoor unsaturated flow experiment. As rates of flux increase, the concentration at the soil surface increases more rapidly.

If volatilization is controlled by the conditions and depth of the boundary layer, the lower humidity and more shallow boundary layer in the outdoor experiments would be expected to maximize volatilization. As a benchmark, for compounds where a dimensionless $K_H$ is much less than $2.5 \times 10^5$, the air boundary layer will form a barrier to chemical loss (Jury et al., 1984). With a calculated value of $K_H$ of $1.15 \times 10^{-4}$, it is reasonable to expect that the relative amount of volatilization in the closed system would have been less than expected in an open system.

A large fraction of the initially applied radioactivity was not recovered (9.4% from the extraction controls, 45.8% from the light-exposed soils, 27.5% in the dark controls) presumably due to binding to the soil resulting in inextractable residues. Miller et al. (1988) found increased mineralization and binding of chlorophenols when irradiated prior to incubation in soils. Photolysis in the presence of $\text{H}_2\text{O}_2$ depleted the nonpolar fraction and produced polar material.
which were highly susceptible to biodegradation, while photolysis alone promoted removal principally by binding. Incorporation of PCP into soil organic matter via oxidative coupling can also occur, in a process similar to that of humic substance synthesis from naturally occurring phenolic compounds (Boyd et al., 1989). These covalently bonded residues are strongly immobilized and stabilized against biodegradation or photolysis.

Irradiation of pentachlorophenol results in the formation of more polar photoproducts, notably tetrachlorocatechol, which may also bind to the soil (Goshal et al., 1992). Weiss et al. (1982) found that $^{14}$C-PCP applied to flooded rice soil in an irradiated plant growth chamber was retained by the soil, with 28.6% present as unidentified inextractable substances after one growth period. Up to 38% was lost by volatilization, with no characterization of radioactivity made. In a second growing period, the portion of inextractable residues increased. Bound residues may not be readily metabolized, and will not reach the sunlit zone. The toxicity of the products, however, is generally reduced, and leaching potential is minimized by sorption.

**SUMMARY COMMENTS**

Photolysis of PCP in soils can be a significant loss mechanism when processes are present to enhance rates of transport into the irradiated zone, although rates of photolysis will be lower than seen in aqueous solution due to
attenuation of light by natural chromophores. As much as 58% of pentachlorophenol was photodegraded in a sandy clay loam soil in 14 days.

Rates of photolysis of PCP in soils can be increased by maintaining high rates of evaporative flux and near saturated conditions, as are expected when depths to water table are small. These processes will result in the translocation of chemicals into the 0.5 mm of the soil surface, where photochemical processes are active. Maintaining near-saturated soil conditions will also minimize volatilization of PCP. Significant contributions of volatilization and biodegradation in the degradation of PCP are anticipated from warm, moist, but unsaturated soils, while little loss by any mechanism is expected in air-dry soils.

REFERENCES


Chapter 5:

Movement and Photodegradation of Napropamide and Imazaquin in Soil Columns With Periodic Infiltration Events
Abstract- Transport and photolysis of two formulated herbicides was measured in two soils. Napropamide or imazaquin was applied to the surface of columns of soil, which were irradiated with ultraviolet light for a four week period. Dark controls were shielded by black plastic. Water was applied to the soils twice weekly to simulate irrigation. The greatest loss from light-exposed columns occurred when imazaquin was applied to a loamy sand soil ("Callahan"), in which no sorption was measured, with 34% less pesticide loss in light exposed soils than in dark controls after 28 days. Downward movement of imazaquin was rapid, but evapoconcentration at the soil surface increased with time, enhancing rates of photodegradation. Little difference between treatments was seen when imazaquin was applied to a sandy clay loam soil ("Montana"). Loss due to photolysis was also noted when napropamide was applied to Montana soil, with 18.3% lost by day 21. Moderate sorption was measured in this soil, and most napropamide remained in the top 1.5 cm of the soil. Less sorption occurred when napropamide was applied to Callahan soil, and redistribution away from the soil surface continued to occur, with no evapoconcentration noted. Results suggest that photolysis will be greatest for very mobile, water soluble compounds, or when surface concentrations are high.
INTRODUCTION

Surface-applied pesticides which absorb light may undergo photolysis, in which the parent compound is transformed into other, often less toxic products (1). Since depth of light penetration is limited to the top 0.5 to 1 mm of the soil surface, due to light screening and attenuation (2), photolysis will only be active if compounds are present within this zone. Processes which transport pesticides from within the soil bulk to the photic zone will increase rates of photodegradation as a function of the amount of time the chemical exists at the atmosphere-soil surface interface.

The effectiveness of transport processes in enhancing rates of photodegradation will depend on properties of the chemical including solubility, vapor pressure and light absorption, and on characteristics of the soil matrix such as particle size distribution and organic matter content. For compounds of relatively high solubility and low vapor pressure, transport with evaporating water will result in upward movement and concentration at the soil surface (3). Rates of downward diffusion or movement with infiltrating water will then determine the amount of time the compound is present in the photic zone.

The work described here examines two herbicides, including imazaquin (2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolinecarboxylic acid) and napropamide (2-(α-naphthoxy)-N,N-diethylpropionamide). Imazaquin is an imidazolinone herbicide used for
broadleaf weed control in soybeans and other legume crops. Imazaquin coated on glass slides or on thin soil layers undergoes rapid photolysis (4). When imazaquin was exposed to ultraviolet (UV) light in aqueous solution, 100% was degraded after 48 hours (5). In moist sand, 45% of applied imazaquin was lost after 48 hours, but less than 10% was lost when applied to air dry sand (5).

Napropamide is a broad spectrum herbicide used in the control of annual grass and broadleaf weeds in many fruit and vegetable crops (6). Properties of napropamide and imazaquin were previously reported in Chapters 2 and 3. Prior work has demonstrated that napropamide is lost rapidly when applied to the soil surface, with apparent first order kinetics (7). Because napropamide is moderately sorbed by most soils, leaching is relatively slow depending on soil properties as well as volumes of water applied (8). When leached with 23 cm of water, as much as 73% of field-applied napropamide remained in the top 10 cm of the soil, although trace concentrations reached depths of 1.8 m (9).

The depth of leaching affects not only potential groundwater contamination, but also the potential for movement to the soil surface and photodegradation of residues. The purpose of this research was to measure relative depths of leaching and upward movement of napropamide and imazaquin in two soils, and to determine whether photolysis continued to occur when pesticides were surface-applied and subjected to periodic infiltration events.
MATERIALS AND METHODS

Chemicals

Devrinol 50DF (54.2% napropamide) was obtained from ICI Americas, Inc. Scepter 70DG (70% imazaquin) was obtained from American Cyanamid Co. These agricultural formulations were used in all experiments. Stock solutions of formulated imazaquin and napropamide were prepared in methanol to 4 mg/mL, and were further diluted with methanol to give a range of standards from 0.4 ug/mL to 40 ug/mL. Stock was stored at 4 °C in amber glass vials sealed with teflon-coated septa.

Soils

Two soils were used in these experiments: “Callahan”, a loamy sand soil, and “Montana”, a sandy clay loam soil, as described in the previous chapters. Soils were passed through a 1 mm sieve and autoclaved prior to use to ensure initial sterility.

Aqueous photolysis

Rates of aqueous photolysis for formulated imazaquin and napropamide were determined under ultraviolet (UV) light using 16 Westinghouse FS40 lamps ($\lambda_{\text{max}} = 310$ nm) as described previously. Stock was diluted in distilled water to concentrations of $8 \times 10^{-5}$ M napropamide and $9 \times 10^{-5}$ M imazaquin. Rates of aqueous photolysis were measured at a distance of 20 cm below the lamps, with
temperatures maintained at 30 °C ± 2 °C. Sampling was performed over a 4 hour period.

Residues were quantified by high performance liquid chromatography (HPLC) using a Hewlett Packard 1050 Liquid Chromatograph as described in Chapters 2 and 3. Photolysis half-lives were calculated by least squares regression of a first order plot of time v. relative concentration.

**Batch equilibrium sorption**

Isotherms for formulated imazaquin and napropamide were measured for both soils using the batch equilibration method as described in Chapters 2 - 4 to determine if sorption equilibria varied from the analytical grade compound to the formulated compound. Five grams of soil was placed in 15 mL test tubes, and eight mL of various concentrations (1.68, 8.4, 16.8, 25.2, and 33.6 ug/mL) of imazaquin dissolved in 0.01 N CaCl₂ were added to the soil. For napropamide, 4 g of soil and 10 mL of solution was used, at concentrations of 1.73, 8.67, 17.3, 26, 34.7, and 43.4 ug/mL. Sorption coefficients were calculated by fitting a linear model to the sorption data, as described previously.

**Soil column photolysis**

Four soil photolysis experiments (each compound on each soil) were conducted under UV light using the FS40 lamps. The experiments were run sequentially, with irradiation of a single soil containing either Devrinol or Scepter
70DG for a 28 day period. Treatments consisted of 14 hours of light exposure per day or no light exposure.

Tall form glass beakers 6.4 cm i.d. by 11.5 cm were used to contain the soils, with two replicate columns per treatment per sampling day for each soil. The beakers were filled to the top with measured amounts of soil, for a bulk density of 1.41/cm³ for Callahan soil, and 1.0 g/cm³ for Montana soil. Solutions of 0.532 mg/mL formulated napropamide and 0.490 mg/mL formulated imazaquin in methanol were prepared, and 3 mL of solution was placed dropwise to cover the surface of the soil. A pulse of 1.5 cm of distilled water was then added to the soil surface at the saturated conductivity of the soil and allowed to infiltrate. Water (1.5 cm) was added twice weekly throughout the 28 day period, with drying of the surface observed between infiltration events. Control samples (4 g soil plus 120 µL of stock and 1 g distilled water) were also weighed into tubes, sealed, covered with aluminum foil, and placed in the light bank to monitor extraction efficiency over the course of the experiment.

Soils which were to be irradiated were placed 20 cm below the FS40 lamps used for the aqueous photolysis experiments. Dark controls were shielded from light by placing black plastic 10 cm above the soil surface. This allowed evaporation to occur in the absence of light. Constant air flow across the soils was maintained by a series of fans, and temperatures were 30 °C ± 2 °C.
Two soil columns for each treatment were sampled on days 7, 14, 21 and 28 of the experiment. A single column was also sampled at the beginning of each experiment to determine the initial distribution in the soil 15 minutes after infiltration of the first pulse of water. The soil was removed from the columns in layers by excavating to the 1.5, 3.5, 5.5, 7.5, 9.5 and 11.5 cm depths. The soil layers were placed in petri dishes and mixed thoroughly to ensure homogeneity. Two 6 g samples were placed in test tubes and stored in the dark at 4 °C until extracted, and the remaining soil was dried at 105 °C for 24 hours for soil moisture determination. On each sampling day, four control samples were also removed from the light bank for extraction and quantification.

Soil samples were extracted using the methods presented in Chapters 2 and 3. Percent of napropamide or imazaquin remaining in each soil layer was calculated on a mass basis relative to the amount applied, and values were normalized by the average recovery from the control samples.

RESULTS AND DISCUSSION

Both napropamide and imazaquin underwent rapid photolysis in aqueous solution, with half-lives of 3.5 (R² = 0.997) and 68.8 min (R² = 0.999) respectively. The respective rate constants were 0.197 and 0.01 min⁻¹. These rates are faster than previously measured for the analytical grade compounds which were irradiated 30 cm below the UV lamps. Measurements made using
analytical grade chemicals at the 20 cm distance showed differences in rates were due to closer placement to the lamps, rather than to differences in the formulations.

The sorption behavior differed widely, as seen in Figure 1, with no sorption of imazaquin measured in Callahan soil, and little in Montana soil, where $K_d = 0.11$ mL/g ($R^2 = 0.996$). This behavior was expected given a soil pH between 7 and 8, with essentially all imazaquin in anionic form, and is similar to coefficients measured for the analytical grade compound (Chapter 3). Much more sorption of napropamide was evident, with values of $K_d$ of 0.74 ($R^2 = 0.994$) and 7.5 mL/g ($R^2 = 0.998$), respectively. These values are essentially the same as those measured in Chapter 2.

The effect of sorption on distribution with depth and retardation of transport can be readily seen in Figures 2 through 5. The greatest mobility was observed when imazaquin was applied to Callahan soil (Figure 2). After the first pulse of water, more than 87% was present below the top 3.5 cm. As much as 35.5% was present at the bottom of the column, suggesting that movement downward to greater depths would occur in longer columns. Some evapoconcentration resulted in increasing amounts in the top 1.5 cm of soil with time. The distribution seen is a function of the closed bottom of the column, and the lack of sorption. In the absence of an impermeable layer, downward redistribution would be expected to continue. Assuming that the bulk of imazaquin present is
Figure 1. Batch equilibrium sorption of napropamide and imazaquin on two soils.
Figure 2. Distribution of imazaquin with depth in Callahan soil with periodic infiltration and irradiation with UV light.
Figure 2. Distribution of imazaquin with depth in Callahan soil with periodic infiltration and irradiation with UV light.
Figure 3. Distribution of imazaquin with depth in Montana soil with periodic infiltration and irradiation with UV light.
Figure 3. Distribution of imazaquin with depth in Montana soil with periodic infiltration and irradiation with UV light.
Figure 4. Distribution of napropamide with depth in Montana soil with periodic infiltration and irradiation with UV light.
Figure 4. Distribution of napropamide with depth in Montana soil with periodic infiltration and irradiation with UV light.
<table>
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</table>

**Figure 5.** Distribution of napropamide with depth in Callahan soil with periodic infiltration and irradiation with UV light.
Figure 5. Distribution of napropamide with depth in Callahan soil with periodic infiltration and irradiation with UV light.
in the soil solution, the data can be regraphed in terms of concentrations in soil solution with depth (Figure 6). Very little difference is seen with depth below the surface layer, where concentrations are very high due to the dryness of the soil.

Downward movement of imazaquin in Montana soil was somewhat slower, reflecting some sorptivity as well as the greater water holding capacity of this soil (Figure 3). Initial movement was confined to the top 5.5 cm following the first pulse of water, with redistribution occurring over time. Essentially no evapoconcentration was noted in the top soil layer.

Redistribution of napropamide with depth was much slower, as expected from the sorption distribution coefficients. In Montana soil, most of the compound remained in the top 1.5 cm throughout the 28 day period, with very slow redistribution downward (Figure 4). The presence of napropamide with depth on day 7, as seen in Figure 4, is presumed to be due to contamination, rather than actual downward migration. Greater movement was seen in the Callahan soil due to less sorption and lower porosity, with continued downward migration over the 4 week period, as seen in Figure 5. No upward evapoconcentration was seen.

Differences in photolysis follow the distribution profiles. When upward movement was marked, or when concentrations in the top profile remained high, differences in amounts lost between dark and light treatments were noted. The greatest loss was measured when imazaquin was applied to Callahan soil, as can be seen in Figure 7, with 34% less left in the light-exposed soils than in the
Figure 6. Distribution of imazaquin with depth in Callahan soil solution with periodic infiltration and irradiation with UV light.
Figure 6. Distribution of imazaquin with depth in Callahan soil solution with periodic infiltration and irradiation with UV light.
Figure 7. Irradiation of imazaquin under UV light on (a) Callahan soil and (b) Montana soil

- □ = light-exposed;  • = dark controls.
dark controls after the 28 day period. Less imazaquin was present in the surface layer of the light-exposed soils than in the dark controls, indicating that photolysis was indeed occurring. In Montana soil containing imazaquin, by the end of the experiment there was some loss from both light-exposed soils and dark controls, with no appreciable difference noted. This suggests that biodegradation may have become the dominant loss mechanism. As seen in Figure 3, essentially no difference was noted in amounts of imazaquin present in the surface layers of the Montana soil treatments, suggesting that little photolysis was occurring.

In the case of napropamide, the scenario was reversed, with continued differences in the light-exposed soils noted only in Montana soil (Figure 8). By day 21, 18.3% less was present in the light-exposed soils than in the dark controls. No additional difference was seen after the final week of the experiment. Less imazaquin was present in the surface layer of the light-exposed soils on days 14 and 21, with only slight differences on day 28. In Callahan soil, a difference of about 6.5% between light-exposed and dark control soils was maintained from days 14 through 21, suggesting that photolysis was not responsible for loss during this time period. The initial difference in masses present in the top 1.5 cm of the soil remained essentially unchanged during the latter part of the experiment.

These results indicate that aqueous photolysis rates are not accurate predictors of rates of photodegradation in soils. The greatest amount of loss
Figure 8. Irradiation of napropamide under UV light on (a) Callahan soil and (b) Montana soil

= light-exposed;  = dark controls.
was seen for imazaquin, which has a half-life almost 20 times slower than napropamide. Factors which are more important seem to be the relative sorption and mobility in the soil, as well as depths of wetting. When no sorption occurs, and adequate moisture is present, movement upward of water soluble, non-volatile compounds can result in increased surface concentrations and thus enhanced rates of photolysis, as was seen with imazaquin in Callahan soil. The magnitude of upward movement, however, was undoubtedly increased by the presence of an artificial impermeable boundary at the 11.5 cm depth. In the absence of this boundary, if the amount of applied water was adequate, depths of leaching would be greater, which would decrease the rate of evapoconcentration at the surface.

Alternatively, if sorption is relatively strong, concentrations near the soil surface will remain high. In the presence of an evaporative flux, water soluble compounds may then move upward into the photic zone, allowing photolysis to occur. This scenario is more realistic, and suggests that rates of photolysis may be greatest when pesticides are moderately sorbed and remain essentially at the soil surface. In either case, it would appear from the results of these experiments that the major contribution of photolysis to loss of soil-applied pesticides will occur initially, with biodegradation playing an increasing role over time.
REFERENCES


Chapter 6.

Concluding Comments

Estimating rates of soil transformation are difficult due to the many parameters that influence the rate of transformation of the compound in the surface 0.5 in of soil. Only compounds that can readily absorb light, as can react with other light-sensitized compounds, will undergo transformation. This research has demonstrated such compounds that are water-soluble and can be transported upward with evaporating water will undergo enhanced rates of photolysis.

Among properties which are important in determining the magnitude of increase in rates is the degree of soil sorption. Sorption retards rates of transport, but also limits downward diffusion out of the light-irradiated zone. In the absence of any sorption, as in the case in an unirradiated zone, was observed in Callahan soil. Downward transport of the compound resulted in redistribution with depth which decreases rate of photolysis. As sorption increases, movement to the soil surface by advection of water becomes much slower, as do rates of photolysis, as was seen in Montane soil. Over a sufficient time period, in the presence of evaporative flux, however, it may be possible to transport some of the compound to the soil surface, and photolysis may continue to be an effective degradation mechanism.

Overall results from the outdoor sunlight soil photolysis experiments are presented in Table 1. These data show that upward movement into the irradiated zone at the soil surface resulted in enhanced rates of photolysis.

When surface-applied and leached into the soil, water-soluble chemicals
Estimating rates of soil photolysis are difficult due to the many processes that influence the nature and availability of the compound in the surface 0.5 mm of soil. Only compounds that can directly absorb light, or can react with other light-sensitized compounds, will undergo transformations. This research has demonstrated such compounds that are water-soluble and can be transported upward with evaporating water will undergo enhanced rates of photolysis.

Among properties which are important in determining the magnitude of increase in rates is the degree of soil sorption. Sorption retards rates of transport, but also limits downward diffusion out of the light-irradiated zone. In the absence of any sorption, as was seen when imazaquin was applied to Callahan soil, downward movement under near-saturated flow conditions resulted in redistribution with depth which decreased rates of photolysis. As sorption increases, movement to the soil surface in solution phase becomes much slower, as do rates of photolysis, as was seen in Montana soil. Over sufficient time periods, in the presence of evaporative flux, however, it may be possible to translocate most of the compound to the soil surface, and photolysis may continue to be an effective degradation mechanism.

Overall results from the outdoor sunlight soil photolysis experiments are presented in Table 1. These data show that upward movement into the irradiated zone at the soil surface resulted in enhanced rates of photolysis.

When surface-applied and watered into the soil, water-soluble chemicals
Table 1. Sunlight photolysis of research chemicals in two soils with differing flow regimes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Callahan Soil</th>
<th>Montana Soil</th>
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<tbody>
<tr>
<td></td>
<td>Near-Saturated Flow</td>
<td>Unsaturated Flow</td>
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<tr>
<td>Napropamide</td>
<td>70 (4) a</td>
<td>71 (2)</td>
</tr>
<tr>
<td>Imazaquin</td>
<td>45</td>
<td>58</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>55</td>
<td>58</td>
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</tbody>
</table>

a Numbers in parentheses represent the range of values of the two experiments conducted at two differing concentrations.
b A major amount of loss occurred in the dark controls, with 23% of pentachlorophenol remaining in Callahan soil, and 40% in Montana soil.

Table 2. Photolysis of research chemicals in two soils with differing flow regimes on Day 14 of Outdoor Experiments

<table>
<thead>
<tr>
<th>Compound</th>
<th>Callahan Soil</th>
<th>Montana Soil</th>
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<td></td>
<td>Near-Saturated Flow</td>
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A major amount of loss occurred in the dark controls, with 23% of pentachlorophenol remaining in Callahan soil, and 40% in Montana soil.

Evaporative flux can then provide a mechanism for upward movement and concentration of solutes at the soil surface. This effect was noted when formulated imazaquin was applied to Callahan soil. Increasing concentrations at the soil surface resulted in the greatest amount of photolysis measured in these experiments, as seen in Table 2. Alternatively, when sorption retained surface-applied napropamide in the top

will redistribute through the soil profile. Depths of penetration of the solute front will depend again on the degree of sorption, and also on properties which influence fluid flow, including the hydraulic potential gradient and the unsaturated hydraulic conductivity. Soil physical properties such as water content, bulk density, porosity, and tortuosity must be considered. Evaporative flux can then provide a mechanism for upward movement and concentration of solutes at the soil surface. This effect was noted when formulated imazaquin was applied to Callahan soil. Increasing concentrations at the soil surface resulted in the greatest amount of photolysis measured in these experiments, as seen in Table 2. Alternatively, when sorption retained surface-applied napropamide in the top
1.5 cm of a Montana soil column, more photolysis was measured than in Callahan soil, where downward redistribution was dominant.

Table 2. Photolysis of research chemicals irradiated with ultraviolet light in two soils with periodic infiltration.

<table>
<thead>
<tr>
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<th>Callahan Soil</th>
<th>Montana Soil</th>
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<tr>
<td>Napropamide</td>
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</tr>
<tr>
<td>Imazaquin</td>
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<td>31</td>
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Chemical properties are also important in assessing the importance of transport on photolysis. For water-soluble, photolabile compounds which are moderately volatile, such as pentachlorophenol, upward transport to the soil surface will also increase rates of volatilization by increasing the concentration at the soil-atmosphere interface. As soil moisture contents decrease, as was seen in the unsaturated flow experiments, solution concentrations increase, as does the fraction of air-filled pores, and the relative rate of volatilization also increases.

Rates of aqueous photolysis are thus not accurate predictors of relative rates of soil photolysis. Properties of the soil matrix and interactions of the chemical with the matrix will have a more profound effect on ultimate rates of photolysis than will half-lives in aqueous solution. The results of this research have shown that transport phenomena in soils must be considered to accurately estimate loss via photolysis.
Structures of Research Chemicals

APPENDIX
Structures of Research Chemicals

NAPROPAMIDE

PENTACHLOROPHENOL

IMAZAQUIN
Competing Processes Governing Rates of Photolysis in Soils
Moisture Retention Functions
measured 12/93 by the hanging water column method

![Graph showing moisture retention functions for Callahan and Montana soils.](image-url)