

9.15

The Geochemistry of Pesticides

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NOMENCLATURE

| | | | |
|------------|---|----------|--|
| $1/n$ | Freundlich exponent (dimensionless) | E_a | activation energy (energy mol ⁻¹) |
| A | Arrhenius preexponential factor (same units as k) | f_{oc} | mass fraction of organic carbon in soil (m m ⁻¹) |
| C_{aq} | concentration of solute dissolved in water (m v ⁻¹) | H | Henry's law constant (various forms) |
| C_{oc} | amount of solute sorbed to soil organic carbon (m m ⁻¹) | k | rate constant for the rate-limiting step of a chemical reaction (units depend on reaction order) |
| C_α | carbon atom representing the site of a particular reaction on a molecule (the "alpha carbon") | K_f | Freundlich partition coefficient (v m ⁻¹) |
| C_β | carbon atom (the "beta carbon") immediately adjacent to C_α | K_{oc} | soil organic carbon–water partition coefficient (v m ⁻¹) |
| | | K_{ow} | octanol–water partition coefficient (dimensionless) |
| | | K_p | soil–water partition coefficient (v m ⁻¹) |

| | |
|-------------|---|
| K_{SA} | soil–air partition coefficient (form depends upon units for H) |
| pK_a | the negative log of the equilibrium constant for the interconversion between a Brønsted acid and its conjugate base (dimensionless) |
| R | universal gas constant (form depends on units for E_a) |
| S_{N2} | bimolecular nucleophilic substitution reaction |
| T | temperature |
| T_{max} | temperature above which substrate decomposition or enzyme inactivation occurs |
| T_{min} | temperature below which biological functions are inhibited |
| T_{opt} | temperature of maximum biotransformation rate |
| μ_{max} | maximum rate of biotransformation ($m\ v^{-1}\ t^{-1}$) |

9.15.1 INTRODUCTION

The mid-1970s marked a major turning point in human history, for it was at that moment that the ability of the Earth's ecosystems to absorb most of the biological impacts of human activities appears to have been exceeded by the magnitude of those impacts. This conclusion is based partly upon estimates of the rate of carbon dioxide emission during the combustion of fossil fuels, relative to the rate of its uptake by terrestrial ecosystems (Loh, 2002). A very different threshold, however, had already been crossed several decades earlier with the birth of the modern chemical industry, which produced novel substances for which no such natural assimilative capacity existed. Among these new chemical compounds, none has posed a greater challenge to the planet's ecosystems than synthetic pesticides, compounds that have been intentionally released into the hydrologic system in vast quantities—several hundred million pounds of active ingredient (a.i.) per year in the United States alone (Donaldson *et al.*, 2002)—for many decades. To gauge the extent to which we are currently able to assess the environmental implications of this new development in the Earth's history, this chapter presents an overview of current understanding regarding the sources, transport, fate, and biological effects of pesticides, their transformation products, and selected adjuvants in the hydrologic system. (Adjuvants are the so-called inert ingredients included in commercial pesticide formulations to enhance the effectiveness of the active ingredients.)

9.15.1.1 Previous Reviews of Pesticide Geochemistry

Pesticides have been in widespread use since the Second World War, and their environmental effects have been of concern for at least four decades (Carson, 1962). As a result, numerous reviews have been published summarizing the results from field and laboratory studies of their distribution, transport, fate, and biological effects in the hydrologic system. The principal features of many of these reviews have been summarized elsewhere for the atmosphere (Majewski and Capel, 1995), vadose zone and groundwater (Barbash and Resek, 1996), surface waters (Larson *et al.*, 1997), stream sediments and aquatic biota (Nowell *et al.*, 1999). Other compilations of existing information on these topics have focused either on particular pesticide classes (e.g., Erickson and Lee, 1989; Weber, 1990; Stamper and Tuovinen, 1998; Laskowski, 2002; Pehkonen and Zhang, 2002; Gunasekara, 2005), or on individual pesticides (e.g., Moye and Miles, 1988; Huber and Otto, 1994). Information on the biological effects of pesticides on both target and nontarget organisms has been extensively reviewed (e.g., Matsumura, 1985; Murphy, 1986; Smith, 1987; Stinson and Bromley, 1991; Howell *et al.*, 1996; Kamrin, 1997; Kegley *et al.*, 1999; Solomon *et al.*, 2000). Valuable overviews of environmental organic chemistry are also available (e.g., Capel, 1993; Schwarzenbach *et al.*, 1993).

9.15.1.2 Scope of This Review

This chapter focuses on the sources, transport, fate, and biological effects of synthetic organic pesticides, their transformation products, and volatile pesticide adjuvants—collectively referred to herein as “pesticide compounds”—in the hydrologic system. Although there are thousands of substances that are currently registered for use as pesticide adjuvants in the United States (USEPA, 2002), discussion of these chemicals will be limited to those that are volatile organic compounds because they are the adjuvant group whose geochemical behavior has been most thoroughly documented. (Volatile organic compounds are commonly used as solvents in commercial pesticide formulations (e.g., Wang *et al.*, 1995).) Most of the pesticide compounds examined in this chapter are registered for use in the United States. Similarly, discussion of the use of these compounds focuses primarily on their applications within the United States. For space considerations, pesticides that are wholly inorganic (e.g., chlorine, sulfur, chromated copper

arsenate, and copper oxychloride), or contain metals (e.g., tributyltin) or metalloids (e.g., arsenicals) are not discussed in detail. Topics for which comprehensive, up-to-date reviews have already been published will receive less attention than those for which fewer reviews are available. Consequently, greater emphasis will be placed on the factors that influence the rates and mechanisms of transformation of pesticide compounds than on the biological effects of these substances, their patterns of use and occurrence, or their partitioning among environmental media.

9.15.1.3 Biological Effects of Pesticide Compounds

All pesticides are designed to kill or otherwise control specific animals or plants, so a great deal is known about the acute biological effects of these chemicals on their target organisms. Insecticides (including most fumigants) act as either physical poisons, protoplasmic poisons, stomach poisons, metabolic inhibitors, neurotoxins, or hormone mimics (Matsumura, 1985). Herbicides control or kill plants through a variety of mechanisms, including the inhibition of biological processes such as photosynthesis, mitosis, cell division, enzyme function, root growth, or leaf formation; interference with the synthesis of pigments, proteins or DNA; destruction of cell membranes; or the promotion of uncontrolled growth (William *et al.*, 1995). Fungicides act as metabolic inhibitors (Matheron, 2001). Most rodenticides are either anticoagulants, stomach poisons, or neurotoxins (Meister, 2000). Because most pesticides are poisons, considerable knowledge has also developed regarding the acute effects of these compounds on humans (e.g., Murphy, 1986).

Far more elusive, however, are the myriad sublethal effects on nontarget organisms (including humans) of chronic exposure to pesticide compounds. Of considerable concern in this regard is endocrine disruption, a phenomenon whose effects were first discovered five decades ago, but whose widespread impacts across a broad range of organisms and ecosystems have become known only since the 1990s (Colborn *et al.*, 1993, 1996; Sumpter and Johnson, 2005), and may be inheritable (Anway *et al.*, 2005). Other effects of chronic pesticide exposure in wildlife—some of which may themselves be related to endocrine disruption—include impaired homing abilities in fish (Scholz *et al.*, 2000), hearing impairment in mammals (Song *et al.*, 2005), eggshell thinning in birds, reduced immune function, liver and kidney damage, teratogenicity, neurotoxicity,

delayed metamorphosis, smaller body size, reduced activity, and reduced tolerance to cold or predatory stress (Murphy, 1986; Smith, 1987; Colborn *et al.*, 1993; Relyea, 2005a; Teplitsky *et al.*, 2005). Ecological effects of pesticide exposure include decreased biodiversity and productivity (Relyea, 2005b) and shifts in predator-to-prey ratios (Relyea *et al.*, 2005; Rohr and Crumrine, 2005). Recent evidence also suggests that many of the malformations and population declines that have been observed in amphibians over the past several decades may have been facilitated by exposure to pesticides at concentrations commonly encountered in the hydrologic system (e.g., Sparling *et al.*, 2001; Hayes *et al.*, 2002; Hayes, 2004; Relyea, 2005c; Hayes *et al.*, 2006). Documented or suspected effects in humans include cancer (Patlak, 1996; Hardell and Eriksson, 1999; Schreinemachers, 2000; Alavanja *et al.*, 2004; Sanborn *et al.*, 2004), immune system suppression (Repetto and Baliga, 1996), impaired neurological development (Colborn, 2006; Eskenazi *et al.*, 2006), learning disorders (Guillette *et al.*, 1998), attention deficit/hyperactivity disorder (ADHD), Gulf War syndrome (Winrow *et al.*, 2003), Parkinson's disease (Brown *et al.*, 2006), fetal death (Bell *et al.*, 2001), earlier onset of puberty (Guillette *et al.*, 2006), birth defects, and shifts in sex ratios (Garry *et al.*, 2002).

Recent biomonitoring studies have provided information on the concentrations of pesticide compounds in the human body, their relations to diet, and their rates of elimination. As part of their third national assessment of exposures to a variety of anthropogenic chemicals and metals in the environment, the Centers for Disease Control and Prevention (2005) reported detection of 29 pesticide compounds in the blood or urine of the US population. For infants and children, most exposures to pesticides appear to come from diet (National Research Council, 1993; Lu *et al.*, 2005). Significantly lower concentrations of organophosphorus (OP) pesticide metabolites, for example, have been measured in the urine of children consuming “organic” fruits, vegetables, and juices (i.e., those produced without the use of synthetic pesticides), relative to those fed the same food items produced conventionally (Curl *et al.*, 2003). Other work has shown that a dietary shift from conventionally grown foods to organic foods results in a statistically significant, rapid decrease (within 1–2 days) in urinary metabolite concentrations for two OP insecticides in children (malathion and chlorpyrifos), with a similarly rapid return to previous levels upon restoration of a conventional diet (Lu *et al.*, 2005).

When, as is often the case, individual pesticides are present in the hydrologic system in combination with other pesticides (e.g., Larson *et al.*, 1999; Kolpin *et al.*, 2000; Squillace *et al.*, 2002; Gilliom *et al.*, 2006), the combined toxicity of the different chemicals may be either antagonistic, additive, or synergistic relative to the effects and toxicities of the individual pesticides alone, depending upon the compounds, organisms, and conditions (e.g., Thompson, 1996; Pape-Lindstrom and Lydy, 1997; Carder and Hoagland, 1998; Howe *et al.*, 1998; Anderson and Lydy, 2002; Belden and Lydy, 2000; Hayes *et al.*, 2006). In addition, pesticide adjuvants may be responsible for substantial increases in the toxicity of commercial formulations, relative to that of the a.i. alone (e.g., Bolognesi *et al.*, 1997; Oakes and Pollak, 1999; Lin and Garry, 2000; Howe *et al.*, 2005; Relyea, 2005c; Renner, 2005). Water-quality criteria that have been established for the protection of aquatic life or human health in relation to individual pesticides, however, do not currently account for the potential effects of transformation products, adjuvants, or other pesticides that may also be present.

9.15.1.4 Variations in Pesticide Use over Time and Space

In 1964, an estimated 617 million pounds of pesticide active ingredients were sold for either agricultural or nonagricultural use in the United States (Figure 1). This amount reached a maximum of 1.14 billion pounds a.i. in 1979 and decreased to 906 million pounds a.i. by 1987 (Donaldson *et al.*, 2002). However, despite overall decreases in total cropland area over the past decade, as well as extensive efforts to reduce pesticide use through the introduction of

integrated pest management practices and genetically engineered crops (US General Accounting Office, 2001), Figure 1 indicates that the total mass of pesticides applied in the United States in 1999 (912 million pounds a.i.) was essentially the same as it was in 1987. Worldwide use in 1999 totalled 5.7 billion pounds of a.i. (Donaldson *et al.*, 2002). Relatively detailed estimates of agricultural pesticide use during the 1990s are available for individual counties across the United States (US Geological Survey, 1998; Thelin and Gianessi, 2000). Estimates of pesticide use in nonagricultural settings, however, are available only on a national scale, despite the fact that such use represented ~23% of the total mass of a.i. sold in the United States in 1999 (Donaldson *et al.*, 2002). Summaries of the agricultural use of specific pesticides in individual countries around the world are available from the Database on Pesticides Consumption, maintained by the United Nations Food and Agriculture Organization (2003).

9.15.1.5 Environmental Distributions in Relation to Use

Figure 2 illustrates the variety of routes by which pesticides are dispersed within the hydrologic system after they are released, either intentionally through application or unintentionally through spills or other accidents. As might be expected, spatial patterns of pesticide detection in air (Majewski *et al.*, 1998), surface waters (Capel *et al.*, 2001), groundwaters (Barbash *et al.*, 1999), bed sediments, and aquatic biota (Wong *et al.*, 2001) have generally been found to correspond with their patterns of application.

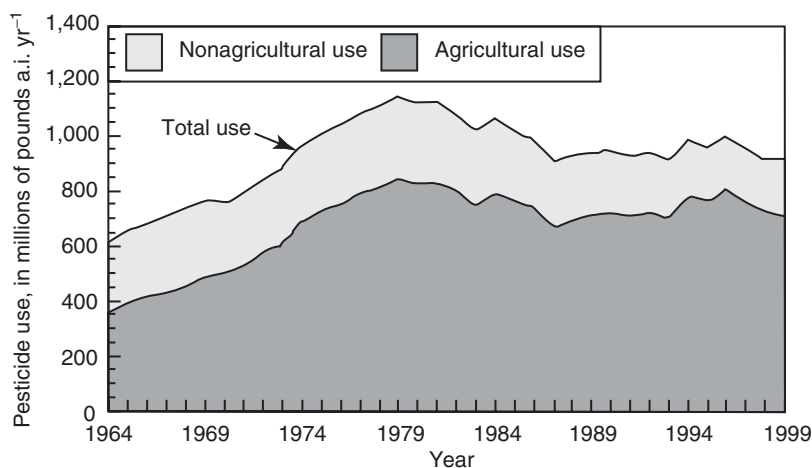


Figure 1 Estimated amounts of pesticides used in the United States for agricultural and nonagricultural purposes from 1964 to 1999. The data were taken from Donaldson *et al.* (2002).

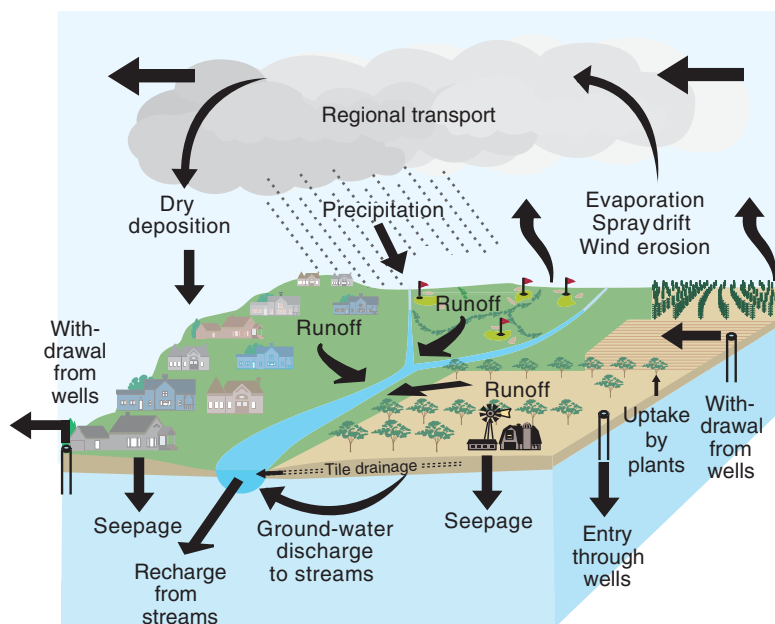


Figure 2 Pesticide movement in the hydrologic system (Barbash and Resek, 1996).

One of the best measures of our ability to predict the spatial distributions of any anthropogenic contaminant in the hydrologic system, however, is the degree to which its total mass can be accounted for after its release into the environment. Mass-balance studies of applied pesticides since the mid-1970s have had only limited success in this regard, even under highly controlled conditions. Of the initial amounts applied during numerous investigations—nearly all of which were conducted in agricultural settings—the proportions of applied a.i. detected in the hydrologic system have typically been 3% or less in surface waters (Wauchope, 1978; Clark and Goolsby, 2000; Capel *et al.*, 2001), 5% or less in vadose zone waters or tile drainage (Flury, 1996), and 5% or less in groundwater (Barbash and Resek, 1996). Estimates of the proportions of applied pesticides that move offsite in spray drift range from 1% to 75% (with considerable variation among different compounds, depending upon their volatility), while the amounts lost to the atmosphere through volatilization from the soil following application have been estimated to be between 0.2% and 90%. Offsite losses through both spray drift and volatilization from soil depend upon a variety of factors such as pesticide properties, application method, formulation, and weather conditions (Majewski and Capel, 1995; Unsworth *et al.*, 1999). High proportions—and often the majority—of the applied mass of pesticide active ingredients have been measured in association with plant tissues and surface soils within the first few hours to days

after application, but the percentages of applied mass detected in these media typically drop below 30% within a few months (Barbash and Resek, 1996). Much of the pesticide mass that has remained unaccounted for during these studies—but did not move offsite in the air, groundwater, or surface waters—may have formed covalent bonds with plant tissues or soil organic matter to form “bound residues” (e.g., Harris, 1967; Nicollie and Donzel, 1994; Xu *et al.*, 2003) or undergone transformation to CO₂ or products for which chemical analyses are rarely conducted (Barbash and Resek, 1996). The fate of applied adjuvants—which usually constitute the majority of the mass of commercial pesticide formulations (Tominack, 2000)—is almost entirely unknown.

9.15.1.6 Overview of Persistence in the Hydrologic System

Given their broad diversity of chemical structures, it is not surprising that pesticide compounds exhibit a wide range of persistence in the hydrologic system. Such variability may be observed among different compounds within a given “environmental medium” (i.e., the atmosphere, water, soil, aquatic sediment, or biological tissues) or for the same compound in different environmental media. Since there are many thousands of compounds that are, or have been used as pesticides, space considerations preclude a characterization of the environmental reactivity of all of them in this

chapter. However, Table 1 provides a brief overview of the persistence of several common herbicides, insecticides, fumigants, and fungicides (representing some of the principal chemical classes of each) in the atmosphere, surface water, soil, and aqueous sediments. These data were taken from Mackay *et al.* (1997), who drew on an extensive body of published data to determine a “half-life class” for 42 pesticide compounds in each of these four environmental media. As will be seen from the discussion in this chapter, the persistence of a given compound in a specific environmental setting is influenced by many different physical, chemical, and biological factors. Each estimate of the half-life class in Table 1 thus represents a generalized mean value selected from what was often a wide range available from previous

studies. Consequently, the reader is referred to Mackay *et al.* (1997) for a summary of the methods by which these data were generated.

The data in Table 1 indicate that the persistence of pesticide compounds generally increases among the four environmental media in the following order: atmosphere < surface waters < soils < aquatic sediments. According to Mackay *et al.* (1997), this pattern is a reflection of several circumstances, including the following: (1) chemical reaction rates in water are generally slower than those in air; (2) pesticides in aquatic sediments and soils are exposed to less sunlight than those in the atmosphere or surface waters, and are therefore less subject to photochemical reactions; and (3) pesticides sorbed to aquatic sediments and soils are often less accessible for biotransformation

Table 1 Persistence of some commonly used pesticides in the atmosphere, surface water, soil, and aquatic sediments.

| Use class | Chemical class | Example(s) | Suggested half-life class in | | | |
|--------------|------------------------|------------------|------------------------------|---------------|------|------------------|
| | | | Atmosphere | Surface water | Soil | Aquatic sediment |
| Herbicides | Acetanilides | Metolachlor | 4 | 6 | 6 | 7 |
| | Amino acid derivatives | Glyphosphate | 4 | 6 | 6 | 7 |
| | Chlorophenoxy acids | 2,4-D | 2 | 3 | 5 | 6 |
| | | 2,4,5-T | 2 | 5 | 5 | 6 |
| | Dinitroanilines | Isopropalin | 2 | 5 | 6 | 7 |
| | | Trifluralin | 4 | 6 | 6 | 7 |
| | Triazines | Atrazine | 1 | 8 | 6 | 6 |
| | | Simazine | 3 | 5 | 6 | 7 |
| | Ureas | Diuron | 2 | 5 | 6 | 7 |
| | | Linuron | 2 | 5 | 6 | 7 |
| Insecticides | Carbamates | Aldicarb | 1 | 5 | 6 | 8 |
| | | Carbaryl | 3 | 4 | 5 | 6 |
| | | Carbofuran | 1 | 4 | 5 | 6 |
| | Organochlorines | Chlordane | 3 | 8 | 8 | 9 |
| | | <i>p,p'</i> -DDT | 4 | 7 | 8 | 9 |
| | | Lindane | 4 | 8 | 8 | 9 |
| | Organophosphates | Chlorpyrifos | 2 | 4 | 4 | 6 |
| | | Diazinon | 5 | 6 | 6 | 7 |
| | | Malathion | 2 | 3 | 3 | 5 |
| | Fumigants | Organochlorines | Chloropicrin | 4 | 3 | 3 |
| Fungicides | Imides | Captan | 2 | 2 | 5 | 5 |
| | Organochlorines | Chlorothalonil | 4 | 4 | 5 | 6 |

Half-life class definitions

| Class | Mean half-life | Range (h) |
|-------|----------------|---------------|
| 1 | 5 h | < 10 |
| 2 | ~ 1 day | 10–30 |
| 3 | ~ 2 days | 30–100 |
| 4 | ~ 1 week | 100–300 |
| 5 | ~ 3 weeks | 300–1,000 |
| 6 | ~ 2 months | 1,000–3,000 |
| 7 | ~ 8 months | 3,000–10,000 |
| 8 | ~ 2 years | 10,000–30,000 |
| 9 | ~ 6 years | > 30,000 |

Source: Mackay *et al.* (1997).

than those in the aqueous phase. The data in Table 1 also suggest that pesticide compounds within the same chemical class may show similar patterns of persistence in a given environmental setting. However, variations in structure among compounds within the same chemical class may also result in substantial variations in reactivity in the same medium (cf. diazinon versus malathion).

9.15.2 PARTITIONING AMONG ENVIRONMENTAL MATRICES

The large-scale movement of persistent pesticide compounds within the hydrologic system is controlled primarily by their rates of advection in water and air masses, as well as by the movement of biota in which they might bioaccumulate. However, the partitioning of these compounds among different environmental media occurs in response to differences in their chemical potential, or “fugacity,” among these media (Mackay, 1979). Given the broad diversity of chemical structures that pesticide compounds encompass, it is not surprising that their affinities for different environmental media also span a wide range. For example, if they are

sufficiently persistent, hydrophobic compounds such as DDT, dieldrin, chlordane, and other organochlorine insecticides (OCs) will, over time, preferentially accumulate in organic soils, lipid-rich biological tissues, and other media with high levels of organic carbon. Similarly, the extent to which pesticide compounds are taken up in the roots of plants generally increases in relation to the affinity of the compounds for lipids (Briggs *et al.*, 1982). By contrast, more volatile compounds, such as chlorofluorocarbons (several of which are, or have been used as adjuvants (Marquardt *et al.*, 1998; USEPA, 2002)) and fumigants, will tend to reside primarily in soil gases and the atmosphere until they degrade. The effects of transformation on the partitioning of pesticide compounds will be discussed in a later section.

Mackay *et al.* (1997) provide detailed examples of fugacity calculations to illustrate how variations in the physical and chemical properties of pesticides affect their partitioning among environmental media. Figure 3 displays the results from some of these calculations for three of the pesticides listed in Table 1. Consistent with the expectations described above, these computations predict that following their release into the hydrologic system,

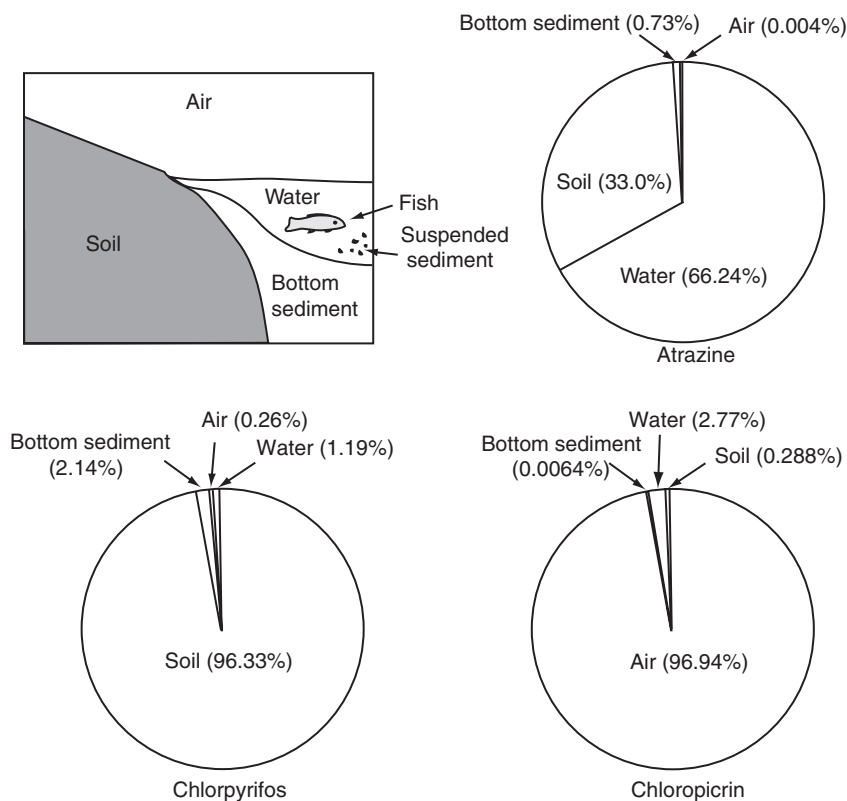


Figure 3 Distributions of atrazine, chlorpyrifos, and chloropicrin among air, surface water, soils, and aqueous sediments, based on fugacity calculations. Percentages sum to <100%, because partitioning into fish and suspended sediment was not accounted for (Mackay *et al.*, 1997).

the relatively water-soluble herbicide atrazine will come to reside mostly in the aqueous phase, the more hydrophobic insecticide chlorpyrifos will tend to concentrate in soil, and the volatile fumigant chloropicrin will be present primarily in the vapor phase. Results from such calculations for a given compound help to focus attention on the media where it is likely to be present in the highest concentrations, and thus where a detailed understanding of its persistence and biological effects may be most critical.

9.15.2.1 Partitioning between Soils, Sediments, and Natural Waters

The movement of pesticide compounds between the solid and aqueous phases exerts considerable influence over the transport, persistence, and bioavailability of these compounds in natural waters. (The “bioavailability” of a compound is the extent to which it is accessible for uptake by living organisms. The term “natural waters” is used herein to refer to water occurring anywhere within the hydrologic system—including precipitation, surface waters, vadose-zone water, and groundwater—regardless of whether or not it has been affected by human activities.) The principal phases among which this partitioning takes place are the aqueous solution itself, natural organic matter (NOM), mineral surfaces, and biological tissues. Because water in the vadose and saturated zones is in such intimate contact with natural solids, such partitioning is presumed to exert a more substantial influence over the movement and persistence of pesticide compounds below the land surface than in surface waters or the atmosphere.

Sorptive interactions with NOM are particularly important for neutral pesticide compounds, including those that are “Brønsted acids” (i.e., chemical species that can donate a hydrogen atom to another species, known as a “Brønsted base” (Stumm and Morgan, 1981)). This is especially true in soils with mass fractions of organic carbon (f_{oc}) of 0.001 or more (Schwarzenbach and Westall, 1981). This threshold, however, is likely to vary inversely with the octanol–water partition coefficient (K_{ow}) among different compounds (McCarty *et al.*, 1981). The discovery that soil–water partition coefficients (K_p) for neutral organic compounds often vary among different soils in direct relation to f_{oc} led to the development of the organic carbon–water partition coefficient, or K_{oc} ($K_{oc} = K_p/f_{oc}$; Hamaker and Thompson, 1972). The association of these compounds with NOM is commonly viewed as being analogous to their dissolution in an organic

solvent, especially since K_{oc} values are known to be inversely related to water solubility, directly related to K_{ow} , and largely independent of competitive effects among solutes (Chiou, 1998, 2002).

Despite their normalization to f_{oc} , K_{oc} values for individual pesticide compounds still vary among different soils and sediments, though to a much lesser extent than K_p values (Curtis *et al.*, 1986). These variations in K_{oc} , which typically span a factor of 10 or less for individual pesticide compounds (e.g., Mackay *et al.*, 1997), are presumed to arise from variations in the sorption properties of the biogenic materials of which NOM is comprised (Shin *et al.*, 1970), changes in the chemical properties of NOM caused by weathering (Chiou, 1998, 2002) or, for ionic compounds or Brønsted acids, variations in solution properties such as pH and salinity (Schwarzenbach *et al.*, 1993).

The exchange of pesticide compounds between aqueous solution and the sorbed phase in soils is not instantaneous. Indeed, the more hydrophobic the compound, the longer the time required to reach the sorption equilibrium. This phenomenon has been attributed to the effect of hydrophobicity on the rate at which an organic molecule diffuses through the polymeric structure of NOM within soil particles or aggregates (Curtis *et al.*, 1986; Brusseau and Rao, 1989). Support for this explanation is provided by the fact that the amount of time required for pesticides to reach sorption equilibrium has been observed to be longer for soils containing higher amounts of NOM (e.g., Moreau and Mouvet, 1997).

A K_p value (and its corresponding K_{oc}) is most commonly determined for a given solute in a specific soil–water system by computing the slope of a “sorption isotherm” (i.e., a graph of sorbed concentration versus dissolved concentration at equilibrium over a range of solute loadings). The widespread use of K_{oc} values assumes that the sorption isotherm is linear, that is, that the quantitative relation between the amount of solute sorbed to the soil organic carbon (C_{oc}) and the dissolved concentration (C_{aq}) is of the following form (Hamaker and Thompson, 1972):

$$C_{oc} = K_{oc}C_{aq}$$

However, the sorption of a number of pesticide compounds to some soils has been found to be more accurately described by the nonlinear Freundlich isotherm (e.g., Hamaker and Thompson, 1972; Widmer and Spalding, 1996), that is,

$$C_{oc} = K_f C_{aq}^{1/n}$$

Published values of Freundlich parameters (K_f and $1/n$) are relatively sparse, but are currently

available for at least 60 pesticide compounds (Barbash, unpublished compilation).

Sorption to mineral surfaces (as opposed to NOM) is generally viewed as more of a displacement than a dissolution phenomenon. Because mineral surfaces tend to be more polar than NOM, sorption to the former is more substantial for polar and ionic compounds than for those that are more hydrophobic (Curtis *et al.*, 1986; Chiou, 1998, 2002). Furthermore, since most NOM and mineral surfaces exhibit either a neutral or negative charge, sorption to soils and sediments is considerably stronger for pesticide compounds that are positively charged in solution—such as paraquat or diquat—than for neutral species, and weaker still for anions. As a consequence, measured K_p values in soils exhibit little dependence upon pH for pesticide compounds that are not Brønsted acids or bases (Macalady and Wolfe, 1985; Haderlein and Schwarzenbach, 1993). However, for those that are Brønsted acids or bases, K_p values increase dramatically as the pH is reduced below the pK_a value(s) for the compound (Haderlein and Schwarzenbach, 1993; Broholm *et al.*, 2001). (The pK_a of a Brønsted acid/base pair is the negative logarithm of the equilibrium constant for their interconversion through the gain or loss of a proton. As such, the pK_a also represents the pH value below which the concentration of the acid exceeds that of the base, and above which the base dominates.) Schellenberg *et al.* (1984) introduced equations that may be used to quantify the effects of pH variations on K_p for Brønsted acids and bases.

Increases in temperature lead to a decrease in K_p values for most pesticide compounds (e.g., Katz, 1993), but some display the reverse trend (Hamaker and Thompson, 1972; Padilla *et al.*, 1988; Haderlein and Schwarzenbach, 1993; Chiou, 1998). In most environmental settings, however, the effect of temperature on sorption is expected to be relatively minor—and, in any event, is nearly always neglected. Precipitation from solution may be significant for some pesticides, as is the case for glyphosate, which has been shown to form relatively insoluble metal complexes with Fe^{III} , Cu^{II} , Ca^{II} , and Mg^{II} at circumneutral pH (Subramaniam and Hoggard, 1988). (Roman numerals are used as superscripts in this chapter to denote the oxidation state of chemical species that may be present either as dissolved ions or as part of the solid phase.)

While much of the preceding discussion has focused on the effect of water–solid partitioning on the movement of pesticide compounds below the land surface, such partitioning may also influence the transport of these chemicals

in surface waters (Figure 4). Compounds exhibiting a pronounced affinity for natural sediments—either because of hydrophobicity, low water solubility, or other chemical characteristics—are transported primarily with suspended sediments in surface waters, rather than in the aqueous phase (Wauchope, 1978). The deposition of sediments to which persistent pesticide compounds are sorbed leads to substantial increases in the residence time of these compounds in aquatic ecosystems. For this reason, detailed analyses of sediment cores obtained from lakes and reservoirs around the country have proved to be useful for observing long-term trends in the concentrations of OCs in aquatic environments over several decades (Van Metre *et al.*, 1998; Van Metre and Mahler, 2005).

In addition to sorption and precipitation, the diffusive exchange of pesticide compounds between “mobile” and “immobile waters” also influences the rates at which these solutes move through the hydrologic system—or, more specifically, through the vadose and saturated zones. (The term “mobile water” refers to subsurface water that moves by comparatively rapid, advective flow along preferred flow paths within soils and other geologic media. By contrast, “immobile water” resides within the interior pores of soil particles and aggregates, and therefore migrates much more slowly, if at all.) This exchange is associated with the macroscopic phenomenon known as “preferential transport,” and can affect solute transport in ways that are similar to the effects of sorption, including the tailing of solute breakthrough curves, long-term uptake and release of solutes over time, and much of what is often erroneously attributed to the formation of bound residues (Barbash and Resek, 1996). The diffusion of pesticide compounds from mobile waters into zones of immobile water is also believed to exert substantial effects on bioavailability, since pesticide molecules may diffuse into the interior pore spaces of soil particles or aggregates and become inaccessible to organisms that might otherwise be able to degrade them (Zhang *et al.*, 1998).

9.15.2.2 Partitioning between Aquatic Biota and Natural Waters

The movement and persistence of pesticide compounds in the hydrologic system are also affected by partitioning and transformation in the tissues of aquatic biota. Pesticide compounds accumulate in aquatic biota as a result of either passive partitioning from the water column or the ingestion of sediment or other

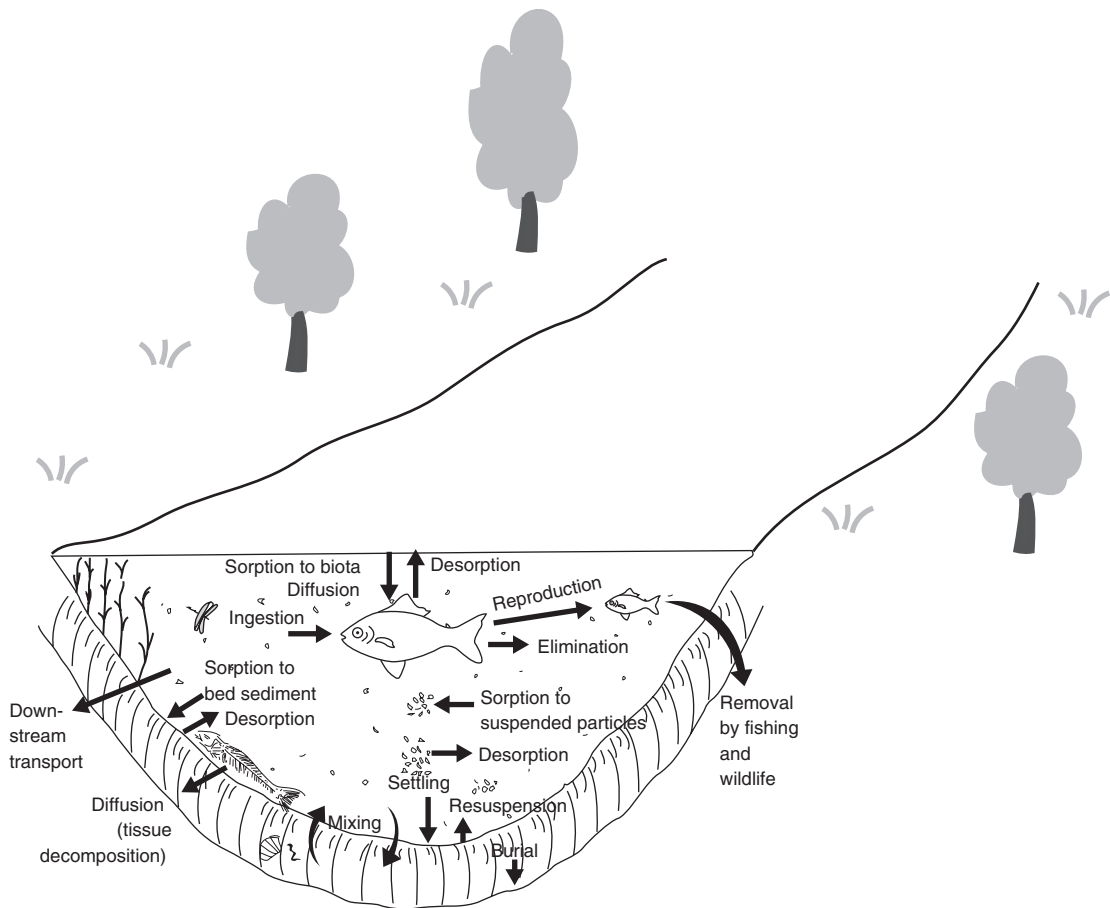


Figure 4 Pesticide movement to, from, and within sediment and aquatic biota in surface waters. Reproduced by permission of Routledge/Taylor & Francis Group, LLC from [Nowell *et al.* \(1999\)](#).

organisms already containing the chemicals. The distribution of pesticides and other organic compounds between water and biological tissues has been most commonly described using a “bioconcentration factor” (BCF). (Compilations of BCF values for pesticides include those assembled by [Kenaga \(1980\)](#) and [Mackay *et al.* \(1997\)](#).) Since both the biota and sediments in aquatic ecosystems are in nearly constant contact with the water itself, the concentrations of pesticide compounds in aquatic sediments have been used as indicators of the anticipated levels of these substances in aquatic biota. This approach, most commonly implemented through the use of a “biota-sediment accumulation factor” (BSAF), has been shown to produce remarkably consistent results for a wide range of aquatic environments and organisms across the United States ([Wong *et al.*, 2001](#)). Partitioning-based approaches for predicting pesticide concentrations in biota, however, do not account for the metabolism of these compounds *in vivo*. [Nowell *et al.* \(1999\)](#) provide a detailed examination of the history,

theoretical basis, assumptions, and limitations of the BSAF model, as well as a comprehensive summary of existing data on the occurrence of pesticide compounds in aquatic fauna and flora across the United States.

9.15.2.3 Partitioning between the Earth’s Surface and the Atmosphere

Several types of observations suggest that atmospheric transport is principally responsible for the fact that pesticide residues are now likely to be detected in every terrestrial and marine ecosystem on the surface of our planet (e.g., [Iwata *et al.*, 1993](#); [Majewski and Capel, 1995](#)). First, as noted earlier, a large proportion of applied pesticide compounds may be transported in the air away from the original application sites as a result of either spray drift, wind erosion of soil, or volatilization from the plant, soil, and water surfaces to which the chemicals were applied ([Majewski and Capel, 1995](#)). (Large-scale movement of migrating

biota may also represent an important—and, in some instances, the most important—mechanism for the global dispersal of pesticide compounds (Ewald *et al.*, 1998; Blais *et al.*, 2005.) Second, while terrestrial and aquatic ecosystems are spatially discontinuous, the atmosphere is a single, comparatively well-mixed medium that is in direct contact with the entire surface of the Earth. Finally, the atmosphere exhibits mixing times that, by comparison with the transformation rates of most of the compounds of interest (e.g., Table 1), are comparatively rapid—on the order of weeks to months for mixing within each of the Northern and Southern Hemispheres, and 1–2 years for exchange between the hemispheres (Majewski and Capel, 1995). However, an understanding of the processes and factors that control the dissemination of pesticide compounds across the globe depends upon a knowledge not only of large-scale spatial patterns of pesticide use (e.g., US Geological Survey, 1998) and atmospheric transport (Majewski and Capel, 1995; Bidleman, 1999; Unsworth *et al.*, 1999), but also of the mechanisms and rates of partitioning of these compounds between air and the materials at the Earth's surface.

9.15.2.3.1 *Movement between air and natural waters*

The parameter used most often to quantify partitioning between air and water, the Henry's law constant (H), takes several forms, but is frequently calculated as the ratio between the vapor pressure and the aqueous solubility of the subcooled liquid. Suntio *et al.* (1988) listed the assumptions upon which the use of H to describe this partitioning is based, described methods for converting between the different forms in which H is expressed, and assembled a compilation of H values for 96 pesticides. The rate of transfer of a pesticide compound between air and water is a function of the contrast between its fugacities in the two phases (Bidleman, 1999). This exchange rate is also controlled by the rates of diffusion of the compound through the thin, adjacent films of air and water that comprise the interface between the two phases, as well as by wind speed, current velocity, turbulence, and the other factors that influence the thickness of these films (Thomas, 1990a).

While it is obvious that pesticide compounds will migrate away from their application sites immediately following their release, the directions of large-scale movement of persistent compounds over longer timescales may be more difficult to anticipate. Fugacity calculations and “enantiomer ratios,” however, have

proved to be valuable tools for revealing the large-scale patterns of atmospheric transport of persistent pesticides. (Enantiomers are pairs of compounds that have the same chemical composition, but spatial arrangements of atoms that differ in such a way that the two molecules are mirror images of one another.) The first of these two methods involves estimating the fugacities of a given pesticide compound in pairs of environmental media that are in intimate physical contact (e.g., air/water or water/soil) to predict its future movement. If the fugacities of the compound in the two media are not equal, their ratio provides an indication of the likely direction of future exchange of the compound between the media of interest.

Enantiomer-based methods exploit the fact that some pesticide compounds are applied in known ratios of enantiomers, most commonly as “racemic” mixtures, that is, 1:1 ratios (Buser *et al.*, 2000; Monkiedje *et al.*, 2003). Although most abiotic transformation and partitioning processes are not affected by the structural differences between enantiomers (Bidleman, 1999), the biotransformation of some pesticide compounds has been found to be an “enantioselective” process, that is, one that exhibits a preference for one enantiomer over the other (e.g., Harner *et al.*, 1999; Monkiedje *et al.*, 2003). Consequently, for a pesticide compound that is applied as a racemic mixture but may undergo enantioselective biotransformation in the environment, an indication of whether or not the compound has undergone biotransformation since it was applied—and thus a rough indication of its residence time in the hydrologic system—may be discerned through the measurement of enantiomer concentration ratios (Bidleman, 1999) or, preferably, enantiomer fractions (Harner *et al.*, 2000).

The use of both fugacity calculations and enantiomer ratios in the Great Lakes, for example, has revealed alternating, seasonal cycles of net deposition and net volatilization of OCs to and from the lake surfaces. However, these methods have also indicated that the concentrations of OCs in the lakes are in approximate long-term equilibrium with the overlying air. Thus, significant reductions in the levels of OCs in the lakes are unlikely to occur until their concentrations in the atmosphere decline. Similar observations have been made in other parts of the world, including Lake Baikal and Chesapeake Bay. Other investigations have indicated that global-scale patterns of deposition for some OCs may be more strongly controlled by temperature than by spatial patterns of application, with net volatilization occurring in more temperate regions and net deposition to soil and other solid surfaces—including snow

and ice—in polar regions (Bidleman, 1999). This pattern of movement, sometimes referred to as “global distillation,” may help explain why such high levels of OCs are commonly detected in polar ecosystems (e.g., Nowell *et al.*, 1999; Wania, 2003; Hermanson *et al.*, 2005).

9.15.2.3.2 Movement between air, soil, and plant surfaces

The volatilization of a pesticide compound from soil is controlled by three general processes (Thomas, 1990b): (1) upward advection in the soil from capillary action caused by water evaporating at the surface (the “wick effect”), (2) partitioning between the solid, liquid, and gas phases within the soil, and (3) transport away from the soil surface into the atmosphere. If a compound is less volatile than water, the wick effect may cause it to concentrate at the soil surface, resulting in its precipitation from solution, an increase in its volatilization rate, and/or a suppression of the water evaporation rate. Thomas (1990b) summarizes a variety of methods that have been devised for estimating the rates of pesticide volatilization from soil following either surface- or depth-incorporated applications. Woodrow *et al.* (1997) found the rates of pesticide volatilization from recently treated soil, water bodies, and “noninteractive” surfaces (including freshly treated plants, glass, and plastic) to be highly correlated with simple combinations of the vapor pressure, water solubility, K_{oc} , and application rates of the compounds of interest.

Pesticides in the vapor phase show considerable affinity for dry mineral surfaces, especially those of clays. However, since mineral surfaces generally exhibit a greater affinity for water than for neutral organic compounds, the vapor-phase sorption of pesticides to dry, low- f_{oc} materials diminishes markedly with increasing relative humidity (RH) as the pesticide molecules are displaced from the mineral surfaces by the adsorbed water (Chiou, 1998, 2002). One important consequence of this phenomenon is that the wetting of dry soils to which a pesticide has previously been applied (and thus sorbed) may lead to a sudden increase in the concentration of the compound in the overlying air (e.g., Majewski *et al.*, 1993). At or above the RH required to cover all of the mineral surfaces with adsorbed water (a water content that some studies suggest is commonly at or below the wilting point), the sorption of pesticide vapor becomes controlled by interactions with the soil organic matter—rather than by competition with water—and the amount of pesticide taken up by the soil depends upon the soil f_{oc} . Organic matter has a much lower affinity for

water than that exhibited by mineral surfaces. As a result, in organic rich soils, f_{oc} exerts considerably more influence over pesticide uptake than does RH, even under dry conditions (Chiou, 1998, 2002). Soil-air partition coefficients (K_{SA}) have typically been computed as the ratio between soil/water and air/water partition coefficients for the compounds of interest (e.g., $K_{SA} = K_p/H$), although methods for the direct measurement of K_{SA} have also been devised (Hippelein and McLachlan, 1998; Meijer *et al.*, 2003).

Consistent with the observations for soil/air partitioning, plant/air partition coefficients for pesticides have been found to be correlated with K_{ow}/H (Bacci *et al.*, 1990). (K_{ow} is commonly used as a measure of partitioning between biological tissues and water.) A direct correlation observed by Woodrow *et al.* (1997) between vapor pressure and the rates of volatilization from the surfaces of recently treated plants suggests that chemical interactions with plant surfaces exert only a minor influence on pesticide volatilization from plants during the first few hours following application. For persistent OCs that were banned in previous decades but are still widely detected in the environment, enantiomer ratios and other methods have been employed to distinguish between inputs from “old” sources—that is, the ongoing atmospheric exchange of these compounds with soils, plants, and surface waters many years after their application—and fresh inputs of the compounds in countries where their use continues, either legally or illegally (Bidleman, 1999).

9.15.3 TRANSFORMATIONS

All transformations of pesticide compounds in the hydrologic system are initiated by either “photochemical” or “thermal” processes, depending upon whether or not the reactions are driven by solar energy. Following its introduction into the environment, the persistence of a pesticide molecule is determined by its chemical structure, as well as by the physical, chemical, and biological characteristics of the medium in which it is located. If it is exposed to sunlight of sufficient intensity within the appropriate wavelength range, the molecule may either be promoted to a higher-energy state and react via “direct photolysis,” or undergo “indirect photolysis” by reacting with another species that has itself been promoted (either directly or indirectly) to a higher-energy level by sunlight.

At the same time, however, the pesticide molecule may also be susceptible to thermal reactions. At a given temperature, the distribution of kinetic

energy among all molecules of a particular chemical species exhibits a specific statistical form known as the “Boltzmann distribution.” For any given reaction, only those molecules possessing a kinetic energy exceeding a specific threshold, the “activation energy,” are likely to undergo that transformation (Atkins, 1982). Thermal reactions are those that occur as a result of collisions between molecules exceeding this energy barrier, either with or without biochemical assistance. Thus, if a pesticide molecule does not react by photolysis (either directly or indirectly), its persistence will be determined by the distribution of kinetic energy among the other chemical species with which it may undergo thermal reactions within the medium of interest.

Because pesticide compounds exhibit such a broad range of chemical structures, the variety of pathways by which they are transformed in the hydrologic system is also extensive, but all may be classified according to the manner in which the overall oxidation state of the molecule is altered, if at all. “Neutral” reactions leave the oxidation state of the original, or “parent” compound unchanged, while “electron-transfer” reactions (also referred to as “oxidation–reduction” or “redox” reactions) involve either an

increase (“oxidation”) or a decrease (“reduction”) in oxidation state. Both neutral and electron-transfer mechanisms have been identified for thermal and photochemical transformations of pesticides. Most of the known transformation pathways involve reactions with other chemical species, but some are unimolecular processes—most commonly those that occur through direct photolysis. In many cases, pesticides may react via combinations of different types of reactions occurring simultaneously, sequentially, or both (e.g., Figure 5). Several previous reviews have provided comprehensive summaries of the pathways that have been observed for the transformation of pesticide compounds in natural systems by either photochemical (e.g., Mill and Mabey, 1985; Harris, 1990b; Atkinson *et al.*, 1999) or thermal mechanisms (e.g., Kearney and Kaufman, 1972; Castro, 1977; Alexander, 1981; Bollag, 1982; Vogel *et al.*, 1987; Kuhn and Sufliata, 1989; Scow, 1990; Coats, 1991; Barbash and Resek, 1996).

Pesticide compounds may be transformed with or without the assistance of living organisms, depending upon compound structure and the biogeochemical environment. Distinguishing between biological and abiotic mechanisms

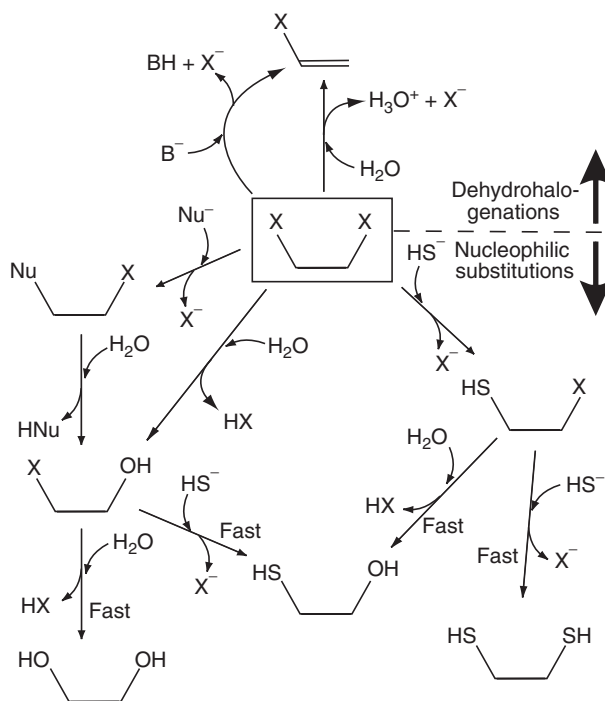


Figure 5 Chemical reactions leading to the dehalogenation of a 1,2-dihaloethane (X = Br for 1,2-dibromoethane (EDB), X = Cl for 1,2-dichloroethane) in an aqueous solution containing the bisulfide anion (HS^-) and one or more additional nucleophiles (Nu^-) that react with the compound via nucleophilic substitution (e.g., nitrate, hydroxide, or a buffer conjugate base), or bases (B^-) that react via dehydrohalogenation (e.g., hydroxide or a buffer conjugate base). After Barbash (1993).

of transformation, however, is not always straightforward. For several pesticide compounds, both abiotic and microbially mediated transformations may occur simultaneously or sequentially (e.g., Skipper *et al.*, 1967; Graetz *et al.*, 1970; Lightfoot *et al.*, 1987; Vogel and McCarty, 1987; Oremland *et al.*, 1994; Gan *et al.*, 1999; Bondarenko *et al.*, 2004). Some transformations may occur either with or without biological assistance (e.g., Wolfe *et al.*, 1986; Jafvert and Wolfe, 1987; Mandelbaum *et al.*, 1993; Loch *et al.*, 2002). Other reactions appear to be primarily, if not exclusively abiotic (Konrad *et al.*, 1967; Haag and Mill, 1988a; Bondarenko *et al.*, 2004). Under the conditions of most natural waters, the “mineralization” of pesticides containing carbon–carbon bonds—that is, their complete conversion into simple products such as CO₂, H₂O, and halide ions—does not take place abiotically (Alexander, 1981), although the abiotic conversion of CCl₄ into a variety of single-carbon products in the presence of dissolved sulfide and clay surfaces has been documented (Kriegman-King and Reinhard, 1992). The cleavage of aromatic rings also does not appear to occur readily through abiotic means in natural waters. With the exception of direct photolysis, however, one or more organisms have been found to be capable of facilitating all of the major types of pesticide transformation reactions listed above (e.g., Kearney and Kaufman, 1972; Castro, 1977; Alexander, 1981; Zepp and Wolfe, 1987; Kuhn and Sufliata, 1989; Scow, 1990; Coats, 1991; Barbash and Resek, 1996).

As noted earlier, transformation reactions of pesticide compounds are typically faster in air than in water (Mackay *et al.*, 1997). However, general trends among the rates of different reactions *per se* are elusive, since chemical structure and the physical, chemical, and biological characteristics of the reaction medium may be as important in determining reaction rate as the nature of the reaction in question. The following discussion describes the circumstances under which pesticide compounds undergo each major type of reaction, and examines the various ways in which the rates of these transformations are controlled by chemical structure and the biogeochemical environment.

9.15.3.1 Photochemical Transformations

Pesticide compounds that may undergo direct photolysis in the hydrologic system are those for which the wavelengths required for bond breakage fall within the range of the solar spectrum (e.g., Zepp *et al.*, 1975). Because of this constraint, relatively few pesticide compounds

undergo direct photolysis; those that have been observed to do so include several chlorophenoxy acids (and their esters), nitroaromatics, triazines, OPs, OCs, carbamates, polychlorophenols, ureas, and fumigants (e.g., Crosby and Leitis, 1973; Dilling *et al.*, 1984; Zepp *et al.*, 1984; Mill and Mabey, 1985; Harris, 1990b; Chu and Jafvert, 1994; Mansour and Feicht, 1994; Lam *et al.*, 2003), as well as fipronil (Walse *et al.*, 2004) and metolachlor (Kochany and Maguire, 1994). Most phototransformations of pesticide compounds occur through indirect photolysis, as a result of reaction with another species, known as a “sensitizer,” or a sensitizer-produced “oxidant.” The most common sensitizers for the phototransformation of pesticide compounds in natural waters include nitrate (Haag and Hoigné, 1985) and the humic and fulvic acids derived from NOM (e.g., Mansour and Feicht, 1994). Sensitizer-produced oxidants include hydrogen peroxide, singlet oxygen, hydroxyl, peroxy, and nitrate radicals, and photoexcited triplet diradicals (Cooper and Zika, 1983; Mill and Mabey, 1985; Mackay *et al.*, 1997). The photoproduction of hydrogen peroxide has also been shown to be catalyzed by algae (Zepp, 1988). In contrast with its tendency to increase the rates of indirect photolysis by acting as a sensitizer, NOM may also inhibit the rates of direct photolysis through light attenuation and, in some cases, the quenching of reactive intermediates (Mill and Mabey, 1985; Walse *et al.*, 2004).

For some pesticide compounds, such as dinitroaniline herbicides (Weber, 1990), phototransformation occurs primarily in the vapor phase, rather than in the dissolved or sorbed phases. Perhaps the most environmentally significant pesticide phototransformation in the atmosphere, however, is the photolysis of the fumigant methyl bromide, since the bromine radicals created by this reaction are 50 times more efficient than chlorine radicals in destroying stratospheric ozone (Jeffers and Wolfe, 1996). Detailed summaries of the rates and pathways of phototransformation of pesticides and other organic compounds in natural systems, and discussions of the physical and chemical factors that influence these reactions, have been presented elsewhere (e.g., Zepp *et al.*, 1984; Mill and Mabey, 1985; Harris, 1990b; Atkinson *et al.*, 1999).

9.15.3.2 Neutral Reactions

The neutral reactions responsible for transforming pesticide compounds in the hydrologic system—listed in roughly decreasing order of the number of compounds known to be

affected—include nucleophilic substitution, dehydrohalogenation, rearrangement, and addition. Figure 6 displays some examples of these reactions for pesticides. Nucleophilic substitution involves the replacement of a substituent on the molecule (the “leaving group”) by an attacking species (the “nucleophile”). (A leaving group is any part of a molecule that is removed during a chemical reaction (March, 1985).) Electrophilic substitution reactions are also well known in organic chemistry (March, 1985). However, since nucleophiles are substantially more abundant than electrophiles in most natural waters, reactions with electrophiles are of relatively minor importance in the hydrologic system, and confined primarily to photolytic and biologically mediated transformations (Schwarzenbach *et al.*, 1993).

Not surprisingly, the nucleophilic substitution reactions that have been studied most extensively for pesticide compounds in natural waters (e.g., Mabey and Mill, 1978; Washington, 1995) are those involving the three solutes that are present in all aqueous systems, that is, H_2O , its conjugate base (OH^-), and its conjugate acid (H_3O^+). These reactions are referred to as “neutral,” “base-catalyzed,” and “acid-catalyzed hydrolyses,” respectively.

The first two of these reactions involve the direct displacement of the leaving group by the nucleophile (H_2O or OH^-), while in the third case, protonation near the alpha carbon (C_α , i.e., the one from which the leaving group is displaced) decreases the electron density on C_α , rendering it more susceptible to nucleophilic attack by H_2O (March, 1985). Some plants employ catalysts to hydrolyze pesticides in their tissues as a detoxification mechanism (Beynon *et al.*, 1972). Extracellular biochemicals that may catalyze the hydrolysis of pesticide compounds include protease, esterase, and phosphatase enzymes (Huang and Stone, 2000). Other microbial enzymes that facilitate pesticide hydrolysis have been summarized by Bollag (1982). As discussed later, metals may also catalyze hydrolysis reactions.

Among the other nucleophiles whose reactions with pesticide compounds may be significant in the hydrologic system, perhaps the most important are reduced sulfur anions (Barbash and Reinhard, 1989a), particularly bisulfide, polysulfides (e.g., Barbash and Reinhard, 1989b; Roberts *et al.*, 1992; Stamper *et al.*, 1997; Miah and Jans, 2001; Lippa and Roberts, 2002; Loch *et al.*, 2002), and thiosulfate (e.g., Ehrenberg *et al.*, 1974; Wang *et al.*,

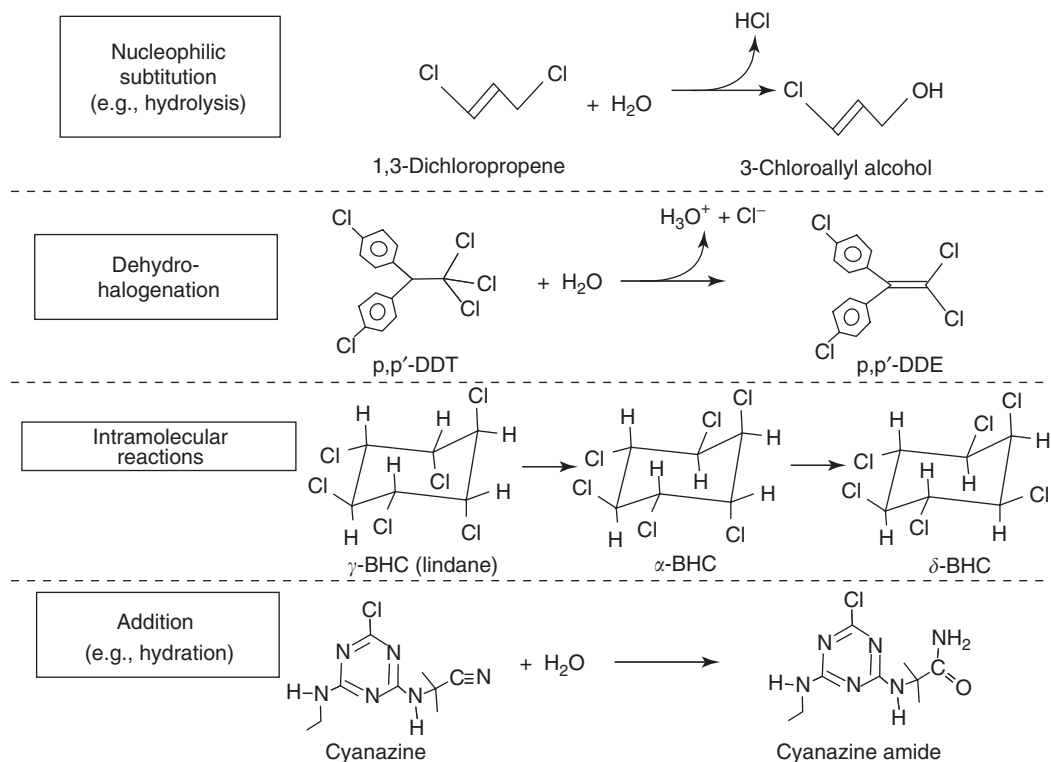


Figure 6 Some examples of neutral reactions of pesticide compounds: nucleophilic substitution (e.g., hydrolysis; Roberts and Stoydin, 1976); dehydrohalogenation (Kuhn and Suffita, 1989); intramolecular reactions (e.g., rearrangement; Newland *et al.*, 1969); and addition (e.g., hydration; Sirons *et al.*, 1973).

2000). Reactions with these nucleophiles are often an indirect mechanism of biotransformation, as these and other reduced sulfur anions are derived primarily from biological activity. However, living organisms also actively employ a variety of nucleophilic enzymes to detoxify halogenated compounds by displacing halide. In addition to the enzyme-catalyzed hydrolyses mentioned earlier, another environmentally important example of these reactions is the displacement of chloride from chloroacetanilide herbicides by glutathione and glutathione-S-transferase (Figure 7) to form the corresponding ethanesulfonic and oxanilic acids (Field and

Thurman, 1996). (The initial step in this example is an illustration of a “synthetic reaction,” or “conjugation,” in which a part of the original molecule is replaced with a substantially larger moiety (Bollag, 1982; Coats, 1991).) Work by Loch *et al.* (2002), however, suggests that the ethanesulfonic acid products might also be generated through abiotic reactions of chloroacetanilide herbicides with reduced sulfur species.

Other nucleophiles of potential importance include pH buffer anions (Figure 5) since, as noted later, buffers are commonly used to stabilize pH during laboratory studies of pesticide transformations. Although it is only a weak

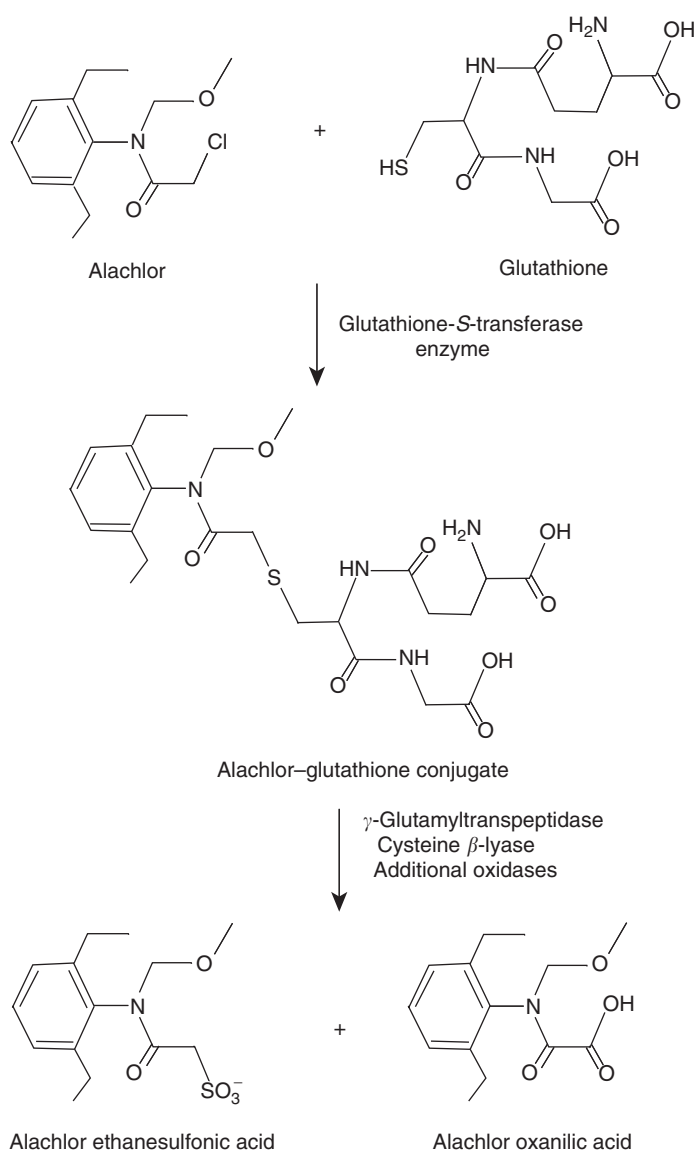


Figure 7 Formation of ethanesulfonic acid and oxanilic acid metabolites from the reaction of a chloroacetanilide herbicide (alachlor) with glutathione and other enzymes. Reproduced by permission of the American Chemical Society from Field and Thurman (1996).

nucleophile, the nitrate anion has also been found (Barbash and Reinhard, 1992b; Barbash, 1993) to displace bromide from the fumigant 1,2-dibromoethane (ethylene dibromide, or EDB) in aqueous solution (Figure 5), an observation worth noting because nitrate is probably the most widespread groundwater contaminant in the world.

Another neutral mechanism by which some pesticide compounds may be transformed is dehydrohalogenation, which involves the removal of a proton and a halide ion (HX) from a pair of adjacent carbon atoms (e.g., Figures 5 and 6). Under the comparatively mild conditions of most natural waters, only singly bonded carbons are likely to undergo this reaction, leading to the formation of the corresponding alkene. Pesticide compounds that have been observed to undergo dehydrohalogenation under environmentally relevant conditions include a number of fumigants, insecticides, and volatile adjuvants (Burlinson *et al.*, 1982; Vogel and Reinhard, 1986; Vogel and McCarty, 1987; Haag and Mill, 1988a; Cline and Delfino, 1989; Jeffers *et al.*, 1989; Kuhn and Sufliata, 1989; Deeley *et al.*, 1991; Barbash and Reinhard, 1992a, b; Ngabe *et al.*, 1993).

Two other neutral mechanisms of pesticide transformation are intramolecular reactions and additions (Figure 6). Intramolecular reactions of pesticide compounds may either leave the overall chemical composition of the parent unchanged (rearrangements (Russell *et al.*, 1968; Newland *et al.*, 1969)), slightly altered (Coats, 1991), or substantially modified (Wei *et al.*, 2000; Wang and Arnold, 2003). Addition reactions involve the coupling of a compound containing a double or triple bond with another molecule; examples involving pesticide compounds include the hydration of cyanazine to form cyanazine amide (Sirons *et al.*, 1973), the hydration of acrolein to form 3-hydroxypropional (Bowmer and Higgins, 1976), and the hypothesized addition of H₂S to polychloroethenes to form the corresponding polychloroethanethiols (Barbash and Reinhard, 1992a; Barbash, 1993).

9.15.3.3 Electron-Transfer Reactions

Thermodynamic considerations dictate that the likelihood with which a pesticide compound in a particular geochemical setting will undergo oxidation or reduction is governed in large part by the tendency of the other chemical species present to accept or donate electrons, respectively (McCarty, 1972). In addition to the more transient oxidants

mentioned earlier in relation to photochemical reactions, those that are most commonly present in natural waters—listed in roughly decreasing order of their tendency to accept electrons—include O₂, NO₃⁻, Mn^{IV}, Fe^{III}, SO₄²⁻, and CO₂. Conversely, the most common reductants in natural waters include CH₄ and other forms of reduced organic carbon, S^{II}, Fe^{II}, Mn^{II}, NH₄⁺, and H₂O (Christensen *et al.*, 2000). Extensive discussion of the chemistry of these and other naturally occurring oxidants and reductants in the hydrologic system has been provided elsewhere in this volume (see Chapters 9.12 and 9.16).

Many redox transformations of pesticide compounds that may take place in the hydrologic system have been observed to occur abiotically (e.g., Kray and Castro, 1964; Castro and Kray, 1966; Wade and Castro, 1973; Mochida *et al.*, 1977; Klecka and Gonsior, 1984; Jafvert and Wolfe, 1987; Tratnyek and Macalady, 1989; Baxter, 1990; Kriegman-King and Reinhard, 1992; Curtis and Reinhard, 1994; Strathmann and Stone, 2001; Carlson *et al.*, 2002; Wang and Arnold, 2003). Among the most common are reactions with both organic and inorganic forms of reduced iron, as well as reactions with reduced forms of nonferrous metals, such as Cr^{II}, Cu^I, Cu^{II}, and Sn^{II}. Reactions with these other metals may be important in natural waters affected by the use of copper-based fungicides or algicides for agriculture, aquaculture, wood preservation, or aquatic weed control; the discharge of mine drainage or tanning wastes; or the use of paints containing organotin fungicides on boats.

While many redox transformations of pesticide compounds can occur abiotically, virtually all such reactions in natural systems are facilitated, either directly or indirectly, by biological processes (Wolfe and Macalady, 1992). Some pesticide compounds may be taken up by living organisms and directly oxidized or reduced through the involvement of a variety of redox-active biomolecules (Bollag, 1982). Enzymes that have been found to be responsible for the biological oxidation of pesticide compounds include methane monooxygenase (Little *et al.*, 1988) and mixed-function oxidases (Ahmed *et al.*, 1980); those involved in reduction reactions consist primarily of transition-metal complexes centered on iron, cobalt, or nickel (e.g., Gantzer and Wackett, 1991; Chiu and Reinhard, 1995). In addition to their ability to oxidize or reduce pesticide compounds directly, living organisms also exert indirect control over these reactions by regulating the predominant terminal electron-accepting processes (TEAPs) in natural waters (Lovley *et al.*, 1994).

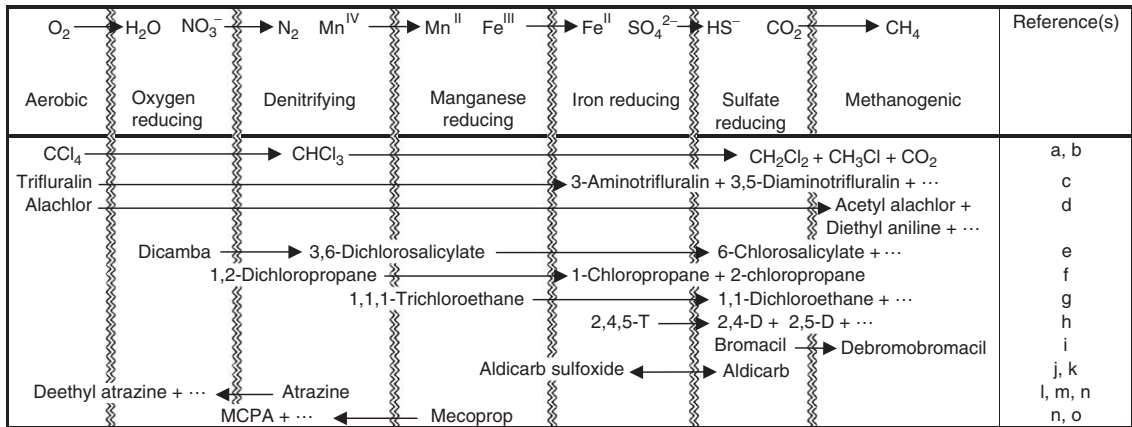


Figure 8 Some examples of electron-transfer reactions of pesticide compounds in relation to dominant terminal electron accepting processes (TEAPs) in natural waters. TEAP sequence based on Christensen *et al.* (2000). Manganese, iron, sulfur, or carbon may be present in either the dissolved or solid phase. Location of each compound indicates the condition(s) under which it has been found to be relatively stable in natural waters. Incomplete lists of transformation products denoted by ellipsis (...); compounds shown are those inferred to have been derived directly from the parent compound. One-way arrows denote essentially irreversible reactions and two-way arrow denotes a reversible reaction. The various references cited are—a: Egli *et al.* (1988); b: Picardal *et al.* (1995); c: Wang and Arnold (2003); d: Novak *et al.* (1997); e: Milligan and Häggblom (1999); f: Tesoriero *et al.* (2001); g: Klecka *et al.* (1990); h: Gibson and Sufliita (1986); i: Adrian and Sufliita (1990); j: Miles and Delfino (1985); k: Lightfoot *et al.* (1987); l: Nair and Schnoor (1992); m: Papiernik and Spalding (1998); n: Rügge *et al.* (1999); o: Agertved *et al.* (1992).

Although a large number of studies have been conducted to examine the persistence of pesticide compounds under the geochemical conditions encountered in soils and natural waters (Barbash and Resek, 1996), relatively few have reported these observations in terms of the dominant TEAPs under which these transformations are likely to occur. Figure 8 summarizes the results from some of the studies from which such information may be extracted. In the figure, the location of each compound indicates the condition(s) under which it has been found to be relatively stable in natural waters. Most of the examples shown involve reductive dehalogenation, reflecting the fact that, as noted by Wolfe and Macalady (1992), most investigations of redox reactions involving pesticides have focused on this type of transformation. For each reaction shown, the shorter the arrow, the more precisely the results from the cited studies could be used to determine the boundary separating the regions of redox stability for parent and product(s). Thus, for example, the specific TEAP under which bromacil undergoes reductive debromination appears to have been more precisely determined than that under which trichloromethane (chloroform) undergoes dechlorination. (Data from other studies not used for the construction of Figure 8, however, may have helped to define these boundaries more precisely.) The figure also shows that the same type of reaction

may require different TEAPs in order for the transformation of different compounds to take place. For example, while the dechlorination of tetrachloromethane to trichloromethane can occur under denitrifying conditions, the dechlorination of 2,4,5-T to 2,4-D and 2,5-D requires sulfate-reducing conditions. Figure 8 also shows that transformations of the same parent compound may yield different products under the influence of different TEAPs (tetrachloromethane, dicamba).

Evidence for the importance of redox conditions in controlling the occurrence of redox-active pesticide compounds in groundwater was provided by a series of statistically significant correlations ($P \leq 0.05$) observed between the concentrations of dissolved oxygen (DO) and those of several volatile organic compounds (VOCs) in shallow groundwater beneath urban areas across the United States. Squillace *et al.* (2004) found that the concentrations of VOCs in which the carbon is relatively oxidized—that is, chloroform, bromodichloromethane (two compounds produced from the use of chlorine for water disinfection, e.g., Ivahnenko and Barbash, 2004) and 1,1,1-trichloroethane (an adjuvant)—exhibited significant positive relations with DO concentrations. By contrast, toluene (also an adjuvant)—in which the carbon is more reduced—showed an inverse relation with DO concentrations. Of particular relevance to

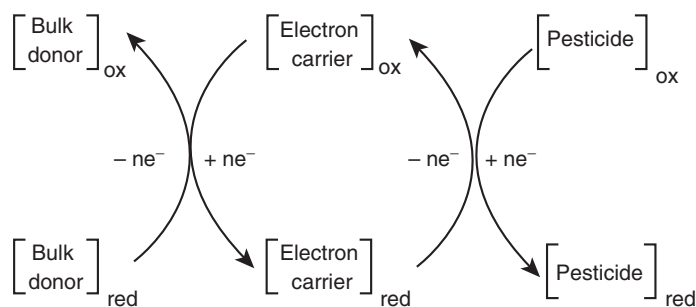


Figure 9 Hypothesized mechanism for the reductive transformation of a pesticide compound through the transfer of electrons from a bulk electron donor (e.g., FeS; Kenneke and Weber, 2003) to a pesticide molecule (e.g., methyl parathion; Tratnyek and Macalady, 1989) by an electron carrier (e.g., hydroquinone; Schwarzenbach *et al.*, 1990). Reproduced by permission of the American Chemical Society from Schwarzenbach *et al.* (1990).

Figure 8 were the observations by Squillace *et al.* (2004) that the concentrations of 1,1-dichloroethane were positively correlated with those of 1,1,1-trichloroethane but inversely correlated with those of DO—suggesting that the presence of 1,1-dichloroethane may have been largely attributable to the reductive dechlorination of 1,1,1-trichloroethane under anoxic conditions.

For neutral reactions, the nature of the attacking species can often be inferred from the composition and structure of the reaction products. By contrast, the specific oxidants or reductants with which pesticide compounds undergo electron-transfer reactions in the hydrologic system are usually unclear (Wolfe and Macalady, 1992). This uncertainty arises both from the variety of different species that can serve as electron donors or acceptors in natural systems (many of which were listed earlier), and from the potential involvement of electron-transfer agents that may act as intermediaries in these reactions (Figure 9). The most common electron-transfer agents (or “electron carriers”) in natural waters appear to be redox-active moieties associated with NOM, since the rates of reduction of pesticides have been found to vary directly with the NOM content of soils (Glass, 1972) and sediments (Wolfe and Macalady, 1992). The specific components of NOM that are responsible for promoting the reduction of pesticide compounds in natural systems are elusive, but laboratory studies have demonstrated that these reactions may be facilitated by several different redox-active moieties likely to be present in NOM (Klecka and Gonsior, 1984; Tratnyek and Macalady, 1989; Schwarzenbach *et al.*, 1990; Gantzer and Wackett, 1991; Curtis and Reinhard, 1994; Chiu and Reinhard, 1995; Garrison *et al.*, 2000; Wang and Arnold, 2003). These moieties are commonly thought to serve primarily as electron carriers in such reactions by cycling back and forth between electron

acceptance from a “bulk” electron donor (e.g., solid-phase iron sulfides (Kenneke and Weber, 2003)) and electron donation to the pesticide compound (Figure 9). However, Glass (1972) proposed an alternate system in which iron serves as the electron carrier, and NOM as the bulk electron donor.

9.15.3.4 Governing Factors

The rates and mechanisms of transformation of a pesticide compound in the hydrologic system are determined by the concentration and structure of the compound of interest (“substrate”), as well as the physical, chemical, and biological circumstances under which each reaction takes place—including the concentrations and structures of other chemical species with which the substrate may react. As might be expected, these factors often show complex patterns of interdependence, such as the simultaneous influence of temperature and soil moisture on reaction rates, or the fact that pH can exert both direct and indirect effects on pesticide persistence. These influences, as well as their interactions, are discussed below.

9.15.3.4.1 Reactant concentrations

Except for intramolecular reactions and direct photolysis, most transformations of pesticide compounds in the hydrologic system are “bimolecular,” that is, their rate-limiting step involves a reaction between the substrate and another chemical species. In natural waters, these other species—which may be of biological or abiotic origin, or associated with the surfaces of natural materials—consist primarily of Brønsted acids and bases, nucleophiles, oxidants, reductants, and catalysts. Although there are some exceptions (e.g., Hemmamda *et al.*, 1994; Huang and Stone, 2000), the rates

of abiotic bimolecular transformation of pesticide compounds in “homogeneous” aqueous solution (i.e., in the absence of a solid phase) have been found to be first-order with respect to the aqueous concentrations of both the substrate and the other reactant—and thus second-order overall—for a wide range of reactions (e.g., Walraevens *et al.*, 1974; Burlinson *et al.*, 1982; Klecka and Gonsior, 1984; Mill and Mabey, 1985; Jafvert and Wolfe, 1987; Haag and Mill, 1988b; Tratnyek and Macalady, 1989; Schwarzenbach *et al.*, 1990; Deeley *et al.*, 1991; Roberts *et al.*, 1992; Curtis and Reinhard, 1994; Wan *et al.*, 1994; Wei *et al.*, 2000; Strathmann and Stone, 2001; Wang and Arnold, 2003). The widespread use of transformation half-lives for quantifying the persistence of pesticide compounds in the hydrologic system, however (e.g., Mackay *et al.*, 1997), is based on the assumption of “pseudo-first-order kinetics” with respect to the substrate, that is, that the concentrations of the other reactants are sufficiently high to remain effectively constant during the transformation of the substrate (Moore and Pearson, 1981). For heterogeneous reactions—which may involve the participation of soil, mineral, or biological surfaces—reaction rates may exhibit a different quantitative relation to the concentrations of the substrate (Zepp and Wolfe, 1987) or the other reactants (Kriegman-King and Reinhard, 1994).

Because the rates of biotransformation are influenced by a variety of factors related to the size, growth, and substrate utilization rate of the microbial populations involved, they often exhibit a more complex dependence upon substrate concentration than do the rates of abiotic transformation in homogeneous solution (D’Adamo *et al.*, 1984). Under many circumstances, however, these more complex relations often simplify to being pseudo first-order with respect to substrate concentration, particularly when the latter is substantially lower than that required to support half the maximum rate of growth of the organisms of interest. At concentrations well above this level, transformation rates may be independent of substrate concentration (Paris *et al.*, 1981).

9.15.3.4.2 Structure and properties of the pesticide substrate

The development of synthetic pesticides has always depended upon an understanding of the effects of chemical structure on the toxicity to the target organism(s). (These effects are discussed in a later section.) However, as the deleterious effects of pesticide compounds on nontarget organisms became more widely

known (e.g., Carson, 1962), it also became increasingly important to learn how the structures of these chemicals control their persistence in the hydrologic system. Indeed, the properties responsible for biological activity are often those that most affect environmental persistence as well (e.g., Scarponi *et al.*, 1991; Smolen and Stone, 1997; Liu *et al.*, 2005). In addition to their direct effects on reactivity (discussed below), variations in chemical structure will also influence persistence indirectly if they shift the partitioning among different phases in which reaction rates are substantially different. Because the ways in which the structure of a pesticide compound controls its reactivity depend, in turn, upon reaction mechanism, these effects will be examined separately for each of the major types of reactions.

Neutral reactions. As noted previously, more studies have been conducted on neutral reactions (especially hydrolysis and dehydrohalogenation) than on other types of reactions involving pesticide compounds in aqueous solution. Thus, it is not surprising that these reactions have also yielded some of the most extensive understanding of the effects of structure on the reactivity of pesticide compounds in the hydrologic system. Investigations of this topic for hydrolysis and dehydrohalogenation have also provided some of the most statistically significant “quantitative structure–reactivity relations” (QSRRs) observed for pesticide compounds (e.g., Wolfe *et al.*, 1978; Roberts *et al.*, 1993; Schwarzenbach *et al.*, 1993).

Several QSRR studies suggest that among the structural features with the greatest influence over hydrolysis rates are those that affect the pK_a of the leaving group. For example, the initial step in OP hydrolysis, which usually occurs at one of the three phosphate ester linkages, involves the displacement of the leaving group with the lowest pK_a (Smolen and Stone, 1997). As a result, for each of five organothiophosphate ester insecticides investigated by Smolen and Stone (1997), the initial product of hydrolysis was always a phenolate anion (Figure 10). This also explains why dimethyl ester OPs, such as methyl parathion and methyl azinphos, hydrolyze more rapidly than their diethyl ester counterparts (Lartiges and Garrigues, 1995). Similarly, for each of the four groups of carbamates (*N*-methyl, *N*-phenyl, *N,N*-dimethyl, and *N*-methyl-*N*-phenyl), the second-order reaction rate constants for base-promoted hydrolysis have been found to be inversely correlated with the pK_a values of the displaced leaving groups (Wolfe *et al.*, 1978). Several of the correlation equations devised for predicting pesticide hydrolysis rates from pK_a values have been compiled by Harris (1990a).

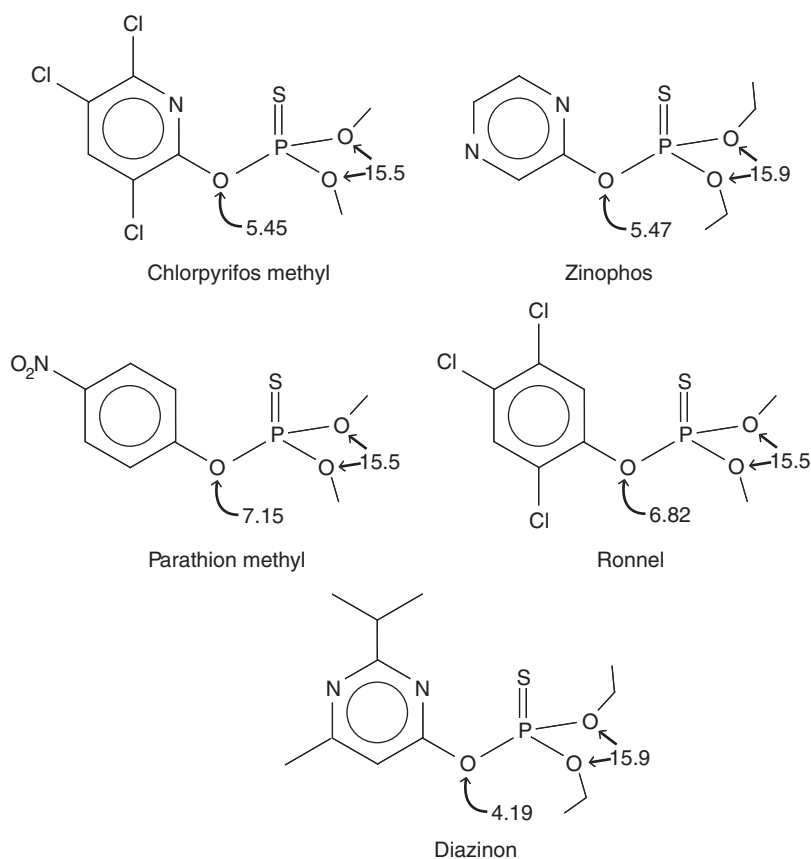


Figure 10 pK_a values for different leaving groups for a series of organothiophosphate insecticides. Leaving group with the lowest pK_a value in each compound is the one first displaced by hydrolysis. Reproduced by permission of the American Chemical Society from [Smolen and Stone \(1997\)](#).

Many other structural effects on the rates of nucleophilic substitution reactions of pesticide compounds have been noted. For example, carbamates with two substituents (other than hydrogen) bound to nitrogen undergo base-promoted hydrolysis more slowly than those with only one ([Wolfe *et al.*, 1978](#)), perhaps as a result of “steric hindrance” (i.e., the enhanced restriction of access to the reaction site by the presence of larger substituents near C_x). Steric hindrance is also believed to be responsible for some of the effects of structure on the rates of acid- and base-catalyzed hydrolysis of chloroacetamide herbicides, particularly the size of the ether or alkyl substituent bound to the amide nitrogen ([Carlson and Roberts, 2002](#); [Carlson, 2003](#)). Data presented by [Scarponi *et al.* \(1991\)](#) suggest that similar factors may affect the rates of nucleophilic substitution reactions between chloroacetamides and glutathione, as well. [Zepp *et al.* \(1975\)](#) observed that the rates of hydrolysis of 2,4-D esters $q(2,4-C_6H_3Cl_2-O-CH_2COOR)$ are higher if R contains an ether linkage near the ester carboxyl group than if R is a hydrocarbon moiety.

The bimolecular nucleophilic (S_N2) displacement of halide from haloalkane adjuvants and fumigants is slowed by the presence of alkyl groups or additional halogen atoms bound to the carbon at (C_x), or immediately adjacent to (C_β) the site of attack. Although bromide is a better leaving group than chloride (i.e., it is displaced more rapidly than chloride), trends in the relative rates of displacement of different halogens may also depend upon the nature of the attacking species, as well as other substituents bound to C_x and C_β . These and other effects of structure on the rates of S_N2 displacement of halide from halogenated pesticide compounds have been examined extensively (e.g., [Barbash and Reinhard, 1989a](#); [Barbash, 1993](#); [Roberts *et al.*, 1993](#); [Schwarzenbach *et al.*, 1993](#); [Stamper *et al.*, 1997](#)).

Since bimolecular dehydrohalogenation reactions are initiated by the abstraction of a hydrogen atom (from C_x) by a Brønsted base, they are promoted by structural factors that increase the ease with which this hydrogen atom can be removed from the molecule, such as the presence of halogens or other “electron-withdrawing” substituents bound to C_x . (These

are moieties that withdraw electron density from the rest of the molecule, the effect being less pronounced with increasing distance from C_α the substituent.) Because this transformation also involves the departure of halide from the adjacent carbon (C_β), rates of reaction are higher for the loss of HBr than for the loss of HCl (e.g., Burlinson *et al.*, 1982; Barbash and Reinhard, 1992a; Barbash, 1993). Roberts *et al.* (1993) provided a comprehensive discussion of these and other effects of structure on the rates of dehydrohalogenation reactions.

Electron-transfer reactions. Although many types of redox reactions involving pesticide compounds have been investigated (Barbash and Resek, 1996), most of what has been learned about the effects of substrate structure and properties on the rates of these reactions in the hydrologic system has come from studies of reductive dehalogenation (e.g., Peijnenburg *et al.*, 1992a) and nitro group reduction (e.g., Schwarzenbach *et al.*, 1993; Wang and Arnold, 2003). Other factors remaining constant, the rates of reductive dehalogenation increase with decreasing strength of the carbon-halogen bond being broken. As a result, the rates of these reactions generally: (1) increase with increasing numbers of halogens on the molecule (e.g., Jafvert and Wolfe, 1987; Gantzer and Wackett, 1991), especially at C_α (Mochida *et al.*, 1977; Klecka and Gonsior, 1984; Butler and Hayes, 2000); (2) decrease among halogens in the order $I > Br > Cl$ (e.g., Kochi and Powers, 1970; Wade and Castro, 1973; Jafvert and Wolfe, 1987; Schwarzenbach *et al.*, 1993); (3) are higher for the removal of halogen from "polyhaloalkanes" (polyhalogenated hydrocarbons lacking multiple carbon-carbon bonds) than from the corresponding "polyhaloalkenes" (polyhalogenated, nonaromatic hydrocarbons with one or more carbon-carbon double bonds) (Gantzer and Wackett, 1991; Butler and Hayes, 2000); and (4) are positively correlated with one-electron reduction potentials (e.g., Gantzer and Wackett, 1991; Curtis and Reinhard, 1994; Butler and Hayes, 2000). A positive correlation of reaction rates with reduction potentials has also been reported for the reduction of nitroaromatic compounds (e.g., Schwarzenbach *et al.*, 1990; Wang and Arnold, 2003). Systematic relations between the rates of reductive dechlorination of polyhaloethanes and electron densities on carbon have also been observed (Salmon *et al.*, 1981).

Rates of reduction may also be influenced by the manner in which different substituents affect the distribution of electrons in the substrate molecule ("electronic" effects), or hinder access to reaction sites (steric effects). Because

the initial, rate-limiting step in most of these reactions involves the addition of an electron to the substrate to form a carbon radical, reaction rates are generally increased by electron-withdrawing groups (e.g., halogens, acetyl, nitro), and decreased by "electron-donating" groups, that is, substituents such as alkyl groups that donate electron density to the rest of the molecule (e.g., Peijnenburg *et al.*, 1992a; Wang and Arnold, 2003). The opposite pattern is expected for rates of oxidation (e.g., Dragun and Helling, 1985). For reactions involving aromatic compounds, electronic effects are substantially more pronounced for substituents located in positions that are either *ortho* or *para* to the substituent being replaced or altered (i.e., either one or three carbons away on the hexagonal aromatic ring) than for those in the *meta* position (i.e., located two carbons away). By contrast, steric effects are most important for substituents in the *ortho* position (Peijnenburg *et al.*, 1992a; Schwarzenbach *et al.*, 1993). These electronic and steric effects on the rates of electron-transfer reactions of pesticide compounds are in agreement with general reactivity theory (March, 1985).

Photochemical reactions. As noted earlier, phototransformations in the hydrologic system occur only for those substrates that either absorb a sufficient amount of light energy within the solar spectrum, or react with photoexcited sensitizers or other photoproduct oxidants. In general, structures that promote light absorption include extensively conjugated hydrocarbon systems (i.e., those possessing alternating double and single bonds), substituents containing unsaturated heteroatoms (e.g., nitro, azo, or carbonyl) and, for substituted aromatics, halo, phenyl, and alkoxy groups (Mill and Mabey, 1985; Harris, 1990b). As with reductive dehalogenation, the rates at which halogenated aromatics undergo photolysis are correlated with the strength of the carbon-halogen bond being broken, as well as with the tendency of other substituents to withdraw electrons or cause steric hindrance (Peijnenburg *et al.*, 1992b). Photolysis rates have also been found (Katagi, 1992) to be correlated with changes in electron density caused by photoinduced excitation (i.e., the promotion of one or more electrons to higher-energy states following the absorption of light energy). A comprehensive summary of the effects of chemical structure on photoreactivity for a broad range of pesticides was provided by Mill and Mabey (1985).

Biotransformations. Some of the structural features that are associated with lower rates of biotransformation include increased branching and decreased length of hydrocarbon chains,

decreased degree of unsaturation, larger numbers of rings in polynuclear aromatic hydrocarbons, the presence of methyl, nitro, amino, or halogen substituents on aromatic rings and, under oxic conditions, increasing numbers of halogens on the molecule (Scow, 1990). As might be expected, many of the ways in which variations in the structure of pesticide compounds affect their rates and mechanisms of biotransformation result from fundamental constraints of structure over chemical reactivity. For example, biotransformation rates among a variety of different pesticides have been found to be linearly correlated with their respective rates of base-catalyzed hydrolysis (Wolfe *et al.*, 1980). Other effects of chemical structure on biodegradability are related more to biological factors than to purely chemical ones. Examples include features that increase the toxicity of the molecule (e.g., additional halogens) or affect the ease with which the appropriate enzyme(s) can access the reaction site (Bollag, 1982). One illustration of the latter effect is the observation, noted earlier, that biochemical reactions are often enantioselective, leading to variations in biotransformation rates among different “isomers” of the same pesticide compound (e.g., Sakata *et al.*, 1986; Peijnenburg *et al.*, 1992a; Falconer *et al.*, 1995; Wong *et al.*, 2002; Monkiedje *et al.*, 2003; Liu *et al.*, 2005). (Isomers are compounds that have the same chemical composition, but slightly different spatial arrangements of atoms. Enantiomers, for example, are isomers that, as noted earlier, are mirror images of one another.) The structural specificity of some biotransformation reactions is also demonstrated by the fact that unequal mixtures of isomers are sometimes produced from the transformation of a single compound (e.g., Parsons *et al.*, 1984).

9.15.3.4.3 Structure and properties of other reactants

The rates and mechanisms of most pesticide transformations in the hydrologic system are, as noted earlier, influenced by the nature of the chemical species reacting with the pesticide compound during the rate-limiting step. These other species participate in the reactions either as Brønsted acids or bases, Lewis acids or bases (electrophiles or nucleophiles, respectively), oxidants, reductants, or catalysts. They may be present in either the aqueous, solid, or gaseous phases, and may be of either abiotic or biological origin. In some cases, individual chemical species may react by different mechanisms simultaneously with the same pesticide compound. For example, Kriegman-King and

Reinhard (1992) observed that in aqueous solution, hydrogen sulfide can react with tetrachloromethane as both a nucleophile (to form carbon disulfide and carbon dioxide) and a reductant (to form trichloromethane, dichloromethane, carbon monoxide, and other products).

Some reactants may play different roles in their interactions with pesticide compounds, depending on the geochemical conditions. Metals and their complexes, for example, may react with pesticide compounds as hydrolysis catalysts (e.g., Mortland and Raman, 1967; Schwanek and Verstraete, 1991; Wan *et al.*, 1994; Smolen and Stone, 1997; Huang and Stone, 2000), direct reductants (e.g., Castro and Kray, 1963, 1966; Mochida *et al.*, 1977; Strathmann and Stone, 2001, 2002a, b), or bulk electron donors through electron-transfer agents such as hydroquinones (e.g., Tratnyek and Macalady, 1989; Curtis and Reinhard, 1994; Wang and Arnold, 2003). Most of what little information is available on how different metals and their complexes vary in their ability to promote transformations of pesticide compounds, however, focuses on their roles as direct reductants or hydrolysis catalysts (see references cited above); reduced iron appears to be the only metal that has been examined as a potential bulk electron donor in natural systems (Glass, 1972; Wang and Arnold, 2003).

A valuable framework for understanding the effects of chemical structure on reactivity is provided by the hard and soft acids and bases (HSAB) model, which classifies Lewis acids and bases as either “hard” or “soft.” Hard acids (e.g., H_3O^+ , Na^+ , Fe^{3+}) and bases (e.g., OH^- , CO_3^{2-} , Cl^-) are relatively small, exhibit low polarizability (and generally high electronegativity), and are more likely to form ionic bonds than covalent ones. Soft acids (e.g., Cd^{2+} , Hg^{2+} , Br_2) and bases (e.g., HS^- , $\text{S}_2\text{O}_3^{2-}$, I^- , CN^-) have the opposite characteristics (Fleming, 1976). Stated simply, the HSAB model posits that hard acids react most readily with hard bases, while soft acids react most readily with soft bases (Pearson, 1972). Thus, the soft base HS^- reacts with the fumigant 1,2-dichloroethane (Figure 11) almost exclusively through nucleophilic substitution at the (soft) carbon bonded to halogen (Barbash and Reinhard, 1989b), while the harder OH^- attacks the same compound primarily at one of the (hard) hydrogens, leading to dehydrochlorination (Walraevens *et al.*, 1974). Similarly, for nucleophilic substitution reactions involving the thionate OPs (see Figure 10 for compound structures), reaction occurs primarily at one of the (soft) carbon atoms bonded to oxygen in the ester linkages when the attacking

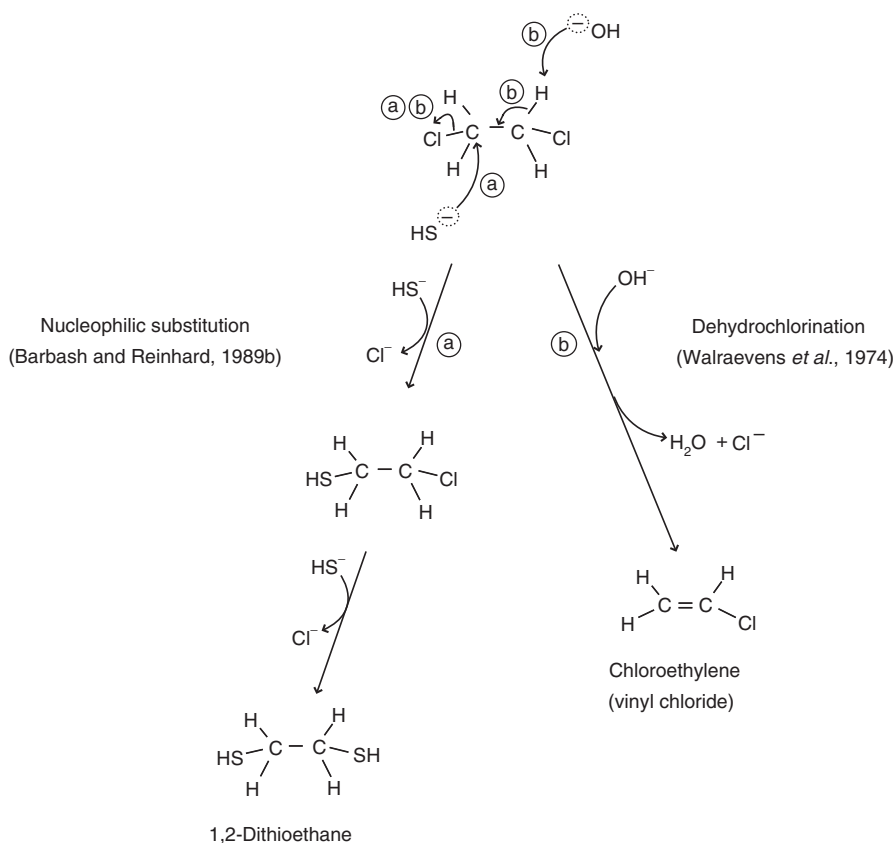


Figure 11 Principal reactions of the fumigant 1,2-dichloroethane with (a) bisulfide (Barbash and Reinhard, 1989b) and (b) hydroxide (Walraevens *et al.*, 1974) in aqueous solution.

species is HS^- (Miah and Jans, 2001), but at the (hard) phosphorus atom when the attacking species is OH^- (Smolen and Stone, 1997). Replacement of (soft) sulfur in thionate OPs with (hard) oxygen in the corresponding oxonate OPs further reduces the electron density on phosphorus, leading to higher rates of hydrolysis (Smolen and Stone, 1997).

Although the HSAB model has been criticized for being insufficiently quantitative (e.g., March, 1985), its predictions have been shown to be consistent with results from frontier molecular orbital calculations for a wide variety of reactions (Klopman, 1968; Fleming, 1976). Such calculations have, in turn, been shown to be useful for elucidating the effects of pesticide structure on reactivity (e.g., Katagi, 1992; Lipka and Roberts, 2002).

In addition to the nature of the “donor atom” (e.g., sulfur in bisulfide versus oxygen in hydroxide), other features that govern the hardness of a nucleophile—and thus the rates and mechanisms of its reaction with pesticide compounds—include the oxidation state of the donor atom and the hardness, size, and structure of the remainder of the molecule. These patterns have been shown to be evident in

reactivity trends observed, for example, among a variety of buffer anions and naturally occurring nucleophiles in their reactions with several haloaliphatic pesticide compounds (Barbash and Reinhard, 1989a; Roberts *et al.*, 1992; Barbash, 1993).

While most applications of the HSAB model have focused on neutral reactions, the model also applies to electron-transfer reactions. The abilities of different transition elements (or other reductants) to reduce a given pesticide compound are generally presumed to increase with their softness—that is, with their ability to donate electrons, a characteristic that is commonly quantified using one-electron reduction potentials (e.g., Schwarzenbach *et al.*, 1993). Reactivity trends reported among different reduced metal cations, however (e.g., Strathmann and Stone, 2001; Mochida *et al.*, 1977), do not precisely track the order of their reduction potentials (Dean, 1985). The relative propensities of different metals to reduce pesticide compounds are therefore influenced by other factors. Related work suggests that such factors include pH and the nature of the coordinating ligand (Strathmann and Stone, 2001, 2002a, b; Mochida *et al.*, 1977).

Comparisons among different metals with regard to their ability to catalyze the hydrolysis of pesticide compounds appear to be limited (e.g., Mortland and Raman, 1967; Smolen and Stone, 1997; Huang and Stone, 2000). Dramatic decreases in reactivity that have been observed upon precipitation at higher pH suggest, however, that metals catalyze hydrolysis much more effectively as ions in solution than as solid-phase (hydr)oxide surfaces (Huang and Stone, 2000).

Ligands have long been known to exert substantial effects upon the solubility, adsorption, and reactivity of transition elements in the hydrologic system. (Indeed, biochemical evolution has taken great advantage of the latter phenomenon, as shown by the critical roles played by metalloenzymes in many metabolic activities.) Several studies have demonstrated the effects of ligand structure on the rates of reductive transformation of pesticide compounds by transition metals, either as dissolved species (e.g., Singleton and Kochi, 1967; Kochi and Powers, 1970; Mochida *et al.*, 1977; Gantzer and Wackett, 1991; Strathmann and Stone, 2001, 2002a, b) or as part of the solid phase (e.g., Torrents and Stone, 1991). One of the studies of greatest relevance to understanding the effect of ligands on the reactivity of pesticide compounds under natural conditions involved an examination by Klecka and Gonsior (1984) of the reductive dehalogenation of polychloroalkanes by ferrous iron in solution. This work indicated that the rates of these reactions are either wholly dependent upon (chloroform, 1,1,1-trichloroethane), or greatly accelerated by (tetrachloromethane) the coordination of the iron with a porphyrin ring (hematin), relative to the rate when iron is coordinated only to water (Fe^{2+}). Huang and Stone (2000) found that the three transition metal cations known to catalyze the hydrolysis of the carbamate insecticide dimetilan (Cu^{II} , Ni^{II} , and Zn^{II}) exhibit strong affinities for nitrogen- and oxygen-donor ligands. Pb^{II} , which did not catalyze this reaction, showed only a weak affinity for these ligands. As might have been expected, different ligands were found to cause varying degrees of catalytic activity for a given metal.

9.15.3.4.4 Physical factors

Temperature. Because both the kinetic energy of molecules and the frequencies of their collisions increase with temperature, so do the rates of thermal reactions, including those that are biologically mediated. By contrast, the rate of photochemical conversion of a molecule from its ground state to an excited state is

not dependent upon temperature. Overall rates of photochemical reaction may, however, exhibit either a positive or a negative dependence on temperature, as the net result of competition among activation, quenching, and reaction steps (Mill and Mabey, 1985). Nevertheless, the detection in Arctic regions of pesticides that exhibit gas-phase lifetimes of only a few days in the more temperate climates where they were likely to have been applied (Bidleman, 1999) demonstrates the importance of accounting for temperature variations, as well as the rapidity of long-range atmospheric transport (mentioned earlier), in predicting the persistence of these compounds in the atmosphere.

The dependence of thermal reaction rates on temperature is most commonly found to be in accordance with the Arrhenius equation

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

where k is the rate constant for the rate-limiting step of the reaction of interest, A the Arrhenius preexponential factor, E_a the activation energy, R the universal gas constant, and T the temperature of reaction (K). As is evident from the form of this equation, the quantities E_a/R and $\ln(A)$ may be estimated from the slope and intercept, respectively, of an Arrhenius plot, that is, a linear regression of $\ln(k)$ versus $1/T$ (e.g., Figure 12). Arrhenius plots exhibiting a significant departure from linearity are usually interpreted to imply the simultaneous operation of more than one transformation mechanism, with different mechanisms dominating over different temperature ranges. Pesticides for which this phenomenon has been observed include 1,2-dibromo-3-chloropropane (Deeley *et al.*, 1991) triasulfuron, and primisulfuron (Dinelli *et al.*, 1998).

The Arrhenius relation will not be observed above the temperature at which the

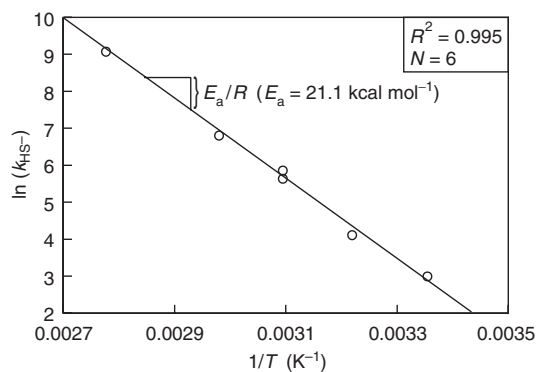


Figure 12 Arrhenius plot for the second-order rate constant (k_{HS^-}) for the nucleophilic displacement of bromide from 1,2-dibromoethane (EDB) by bisulfide ion (HS^-). After Barbash (1993).

decomposition or, as may occur for enzymes, inactivation of one or more of the reactants occurs (T_{\max}). Indeed, adherence to this relation at temperatures well above T_{\max} for most microorganisms has been used as evidence for an abiotic, rather than a biologically mediated mechanism of transformation (Wolfe and Macalady, 1992). For biotransformations, the Arrhenius equation also fails to describe the temperature dependence of reaction rates below the temperature at which biological functions are inhibited (T_{\min}), and above the temperature of maximum transformation rate (T_{opt}). An empirical equation introduced by O'Neill (1968) may be used to estimate the rates of biotransformation as a function of ambient temperature, T_{\min} , T_{opt} , T_{\max} (in this case, the lethal temperature), E_a , and the maximum biotransformation rate (μ_{\max}). Because of the complexity of biochemical systems and the myriad of different structures encompassed by pesticide compounds, T_{\min} , T_{opt} , T_{\max} , E_a , and μ_{\max} are all likely to vary among different compounds, microbial species, and geochemical settings (e.g., Gan *et al.*, 1999, 2000). However, Vink *et al.* (1994) demonstrated the successful application of the O'Neill function to describe the temperature dependence of biotransformation for 1,3-dichloropropene and 2,4-D in soils (Figure 13).

Although the dependence of reaction rates on temperature has been well known for over a century (Moore and Pearson, 1981), the temperatures at which transformation half-lives are measured are often not reported, either by the original publications or in data compilations (e.g., Nash, 1988; USDA/ARS, 1995; Pehkonen and Zhang, 2002). Similarly, as noted by Barbash and Resek (1996), the effects of temperature variations on transformation rates are rarely incorporated into simulations of

pesticide fate in the hydrologic system. Several studies, however, have demonstrated the importance of adjusting transformation rates for seasonal and depth-related variations in temperature when predicting pesticide persistence (Watson, 1977; Padilla *et al.*, 1988; Wu and Nofziger, 1999; Beulke *et al.*, 2000). As is evident from the Arrhenius equation, the adjustment of pesticide transformation rates for variations in temperature requires the availability of data on E_a for the compound and setting of interest. Compilations of E_a values appear to be rare in the literature, but a few summaries are available for the transformations of a variety of herbicides (Nash, 1988; Smith and Aubin, 1993), adjuvants, and fumigants (Barbash, 1993), as well as for the activity of soil enzymes known to effect pesticide transformations (Wu and Nofziger, 1999). E_a values—or data from which they may be computed—are currently available for at least 83 pesticide compounds in the published literature (Barbash, unpublished compilation).

Soil moisture content. Rates of pesticide transformation in soils have usually been found to increase with moisture content up to the “field capacity” of the soil (e.g., Burnside and Lavy, 1966; Roeth *et al.*, 1969; Walker, 1974; Anderson and Dulka, 1985; Walker, 1987; Cink and Coats, 1993). (Field capacity is the amount of water remaining in a soil after the rate of gravity drainage becomes negligible.) This dependence has been described through the use of an empirical equation, introduced by Walker (1974), that expresses transformation half-life as an inverse exponential function of soil moisture content (up to field capacity). The Walker equation has been used to quantify the effects of soil moisture on the rates of transformation of atrazine (Rocha and Walker, 1995), propyzamide, napropamide (Walker, 1974), and at least 25 other pesticide compounds (Gottesbüren, 1991). Similarly, Parker and Doxtader (1983) found that the rate of transformation of 2,4-D in a sandy loam increased with decreasing soil moisture tension, but observed an exponential relation between the two variables that was different from that implied by the Walker equation.

The dependence of pesticide transformation rates on soil moisture is commonly assumed to reflect the influence of water content on biotransformation. For example, Parker and Doxtader (1983) attributed the moisture dependence of 2,4-D transformation rates to two different effects of reduced soil moisture on biological processes, that is, (1) reduced activity of microbial populations and (2) higher pesticide concentrations, which have been shown by other investigators (e.g., Cink and Coats, 1993)

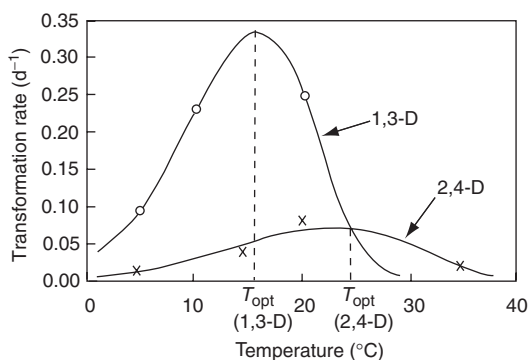


Figure 13 Variations in the rates of biotransformation of 1,3-dichloropropene (1,3-D, circles) and 2,4-D (crosses) with temperature in soils, fitted to the O'Neill function. Reproduced by permission of Wiley on behalf of the SCI from Vink *et al.* (1994).

to inhibit microbial degradation. For soil moisture contents above field capacity, however, this relation might not be observed, especially for aerobic transformations that may be inhibited in saturated soils following the consumption of dissolved oxygen. Abiotic factors may also be involved, since a direct relation between pesticide transformation rates and soil moisture has been observed in sterile soils, as well (Anderson and Dulka, 1985). Furthermore, some nonbiological processes may exhibit the opposite effect; both the Lewis and Brønsted acidity of mineral surfaces—and thus their tendency to promote the oxidation or acid-catalyzed reactions of pesticide compounds, respectively—are enhanced with decreasing soil moisture (Voudrias and Reinhard, 1986).

Interactions among temperature, moisture, and soil texture. The effects of variations in temperature and moisture content on the rates of pesticide transformation in soil show a complex interdependence, the nature of which may vary among different compounds for the same soil, as well as among different soils for the same compound (Walker, 1974; Nash, 1988; Baer and Calvet, 1999). Equations used to describe the simultaneous effects of temperature and soil moisture on pesticide transformation rates have been reported by Parker and Doxtader (1983) and Dinelli *et al.* (1998, 2000). In a comprehensive review of 178 studies that compared observed pesticide concentrations in soils with those predicted using a pesticide persistence model, Beulke *et al.* (2000) demonstrated the importance of accounting for spatial and temporal variations in temperature and moisture in estimating the rates of pesticide transformation. Interactions between abiotic and biological factors are likely to be responsible for the observation that the nature of the relation between soil moisture and the rates of pesticide transformation may, in turn, depend upon soil texture (e.g., Rocha and Walker, 1995; Gan *et al.*, 1999). Rocha and Walker (1995) also observed that the effect of temperature on atrazine transformation could be a function of soil texture, as well.

Solar energy input. For pesticide compounds that undergo phototransformation in natural waters, the rate of reaction is controlled by a number of factors that affect the amount of light energy reaching the reactant(s) of interest. These include the “irradiance,” or the rate of energy input from the Sun (which, in turn, is controlled in part by latitude, season, and time of day) at the wavelengths of maximum light absorption for each reactant, as well as turbidity, color, and depth within the water body of interest. While the presence of suspended solids is generally presumed to reduce photolysis rates

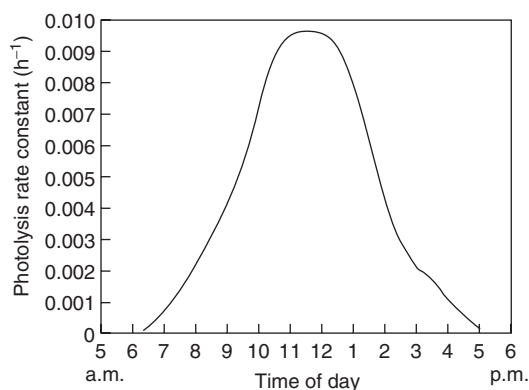


Figure 14 Dependence of the rate constant for the photolysis of 2,4-D butoxyethyl ester (in water at 28 °C) on the time of day in the southern United States. Reproduced by permission of the American Chemical Society from Zepp *et al.* (1975).

in surface water through light attenuation, in some instances the presence of suspended sediments has been observed to increase the rates of these reactions. This phenomenon has been attributed to forward scattering of the incident light by the suspended particles, which can result in an increase in the light path length (Miller and Zepp, 1979; Mill and Mabey, 1985). The effects of various physical and chemical factors on the rates of photochemical transformation of pesticide compounds have been summarized by Mill and Mabey (1985) and Harris (1990b). Zepp *et al.* (1975) presented graphical illustrations of how the rate of 2,4-D butoxyethyl ester photolysis varies with time of day (in Athens, GA; Figure 14), season, and latitude in the Northern Hemisphere (Figure 15).

9.15.3.4.5 Geochemical environment

As is the case for its physical properties, the geochemical characteristics of the reaction medium can also influence the rates and mechanisms of pesticide compound transformation in the hydrologic system, as well as the health and activity of the organisms capable of transforming these compounds. Such characteristics include redox conditions (discussed earlier), pH, ionic strength, the structure and concentrations of any surface-active substances (SAS), solvents or ligands that may be present, and the chemical properties of any interfaces with which the reactants may come in contact.

pH. Changes in pH can affect the rates of pesticide compound transformation in both direct and indirect ways. Direct effects arise from the fact that shifts in pH reflect changes in the concentrations of two potentially important reactants that are present in all aqueous

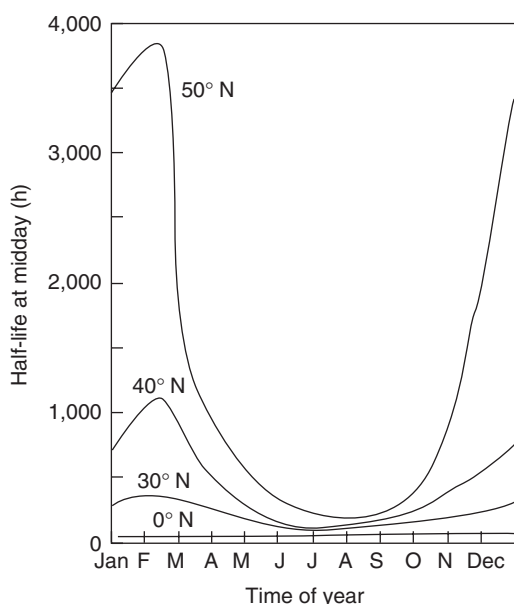


Figure 15 Dependence of the half-life for the photolysis of 2,4-D butoxyethyl ester (in water at 28 °C) on season and northern latitude. Reproduced by permission of the American Chemical Society from [Zepp *et al.* \(1975\)](#).

solutions, that is, H_3O^+ and OH^- . However, pH changes may also exert substantial indirect effects on pesticide transformations, through their influence on biological activity (e.g., [Mallat and Barceló, 1998](#)), the surface properties of reactive natural solids such as manganese oxides ([Baldwin *et al.*, 2001](#)) and clays ([Voudrias and Reinhard, 1986](#)), and the concentrations of other reactants. For pesticide compounds that are Brønsted acids or bases, such as the sulfonylurea herbicides ([Smith and Aubin, 1993](#)), variations in pH may influence transformation rates in solution if the reactivities of the conjugate acid and base are substantially different from one another.

Even if the aqueous concentration of a pesticide compound is independent of pH, however (as is the case for most parent compounds), its transformation rate may still vary with changes in pH if the attacking species is a Brønsted acid or base. In such instances, the pH dependence of the reaction rate will parallel that of the attacking species concentration. For pesticide compounds, this effect has been reported for nucleophilic substitution reactions involving H_3O^+ , OH^- (e.g., [Mabey and Mill, 1978](#)), and HS^- ([Haag and Mill, 1988b](#); [Roberts *et al.*, 1992](#); [Lippa and Roberts, 2002](#)), for reduction ([Strathmann and Stone, 2002a, b](#); [Wang and Arnold, 2003](#)) or hydrolytic catalysis by divalent metal cations ([Huang](#)

[and Stone, 2000](#)), and for reduction by model compounds employed to mimic the electron-transfer capabilities of hydroquinone moieties found in NOM ([Tratnyek and Macalady, 1989](#); [Curtis and Reinhard, 1994](#)). Indeed, the latter observation may explain why the reduction of methyl parathion in anoxic sediments was reported by [Wolfe *et al.* \(1986\)](#) to occur more rapidly under alkaline conditions ($8 < \text{pH} < 10$) than under acidic conditions ($2 < \text{pH} < 6$). The relative rates among competing photochemical transformations for individual pesticide compounds may also shift with pH. [Crosby and Leitis \(1973\)](#), for example, observed pH-related shifts in the yields of different products from the aqueous photolysis of trifluralin, both in the presence and the absence of soil ([Figure 16](#)).

The overall rate at which a pesticide compound undergoes hydrolysis in water represents the sum of the rates of the acid-catalyzed, neutral, and base-catalyzed processes ([Mabey and Mill, 1978](#)). For those pesticide compounds that react only with H_2O , the rate of hydrolysis is independent of pH (e.g., [McCall, 1987](#); [Hong *et al.*, 2001](#)). Some pesticide compounds, however, react with more than one of the three species of interest (H_3O^+ , H_2O , and/or OH^-), resulting in a pattern of pH dependence that may display an abrupt shift above or below a particular threshold pH value ([Mabey and Mill, 1978](#); [Schwarzenbach *et al.*, 1993](#)). Few compilations of these threshold parameters appear to be available for pesticide compounds ([Mabey and Mill, 1978](#); [Mabey *et al.*, 1983](#); [Roberts *et al.*, 1993](#); [Schwarzenbach *et al.*, 1993](#)), but individual values may sometimes be inferred from published data (e.g., [Zepp *et al.*, 1975](#); [Burlinson *et al.*, 1982](#); [Bank and Tyrrell, 1984](#); [Weintraub *et al.*, 1986](#); [Lightfoot *et al.*, 1987](#); [Cline and Delfino, 1989](#); [Jeffers *et al.*, 1989](#); [Lee *et al.*, 1990](#); [Ngabe *et al.*, 1993](#)). Other results suggest that these threshold parameter values may vary with temperature ([Lightfoot *et al.*, 1987](#)).

The dependence of transformation rate on pH is not always consistent among pesticides within the same chemical class. For example, while the hydrolysis reactions of most OP ([Konrad and Chesters, 1969](#); [Konrad *et al.*, 1969](#); [Mabey and Mill, 1978](#)) and carbamate insecticides ([Wolfe *et al.*, 1978](#)) are primarily base-catalyzed, both diazinon ([Konrad *et al.*, 1967](#)) and carbosulfan ([Wei *et al.*, 2000](#)) are also subject to the acid-catalyzed reaction. Summaries of the pH dependence of hydrolysis rates for a variety of pesticides have been provided by [Mabey and Mill \(1978\)](#), [Bollag \(1982\)](#), [Schwarzenbach *et al.* \(1993\)](#), and [Barbash and Resek \(1996\)](#).

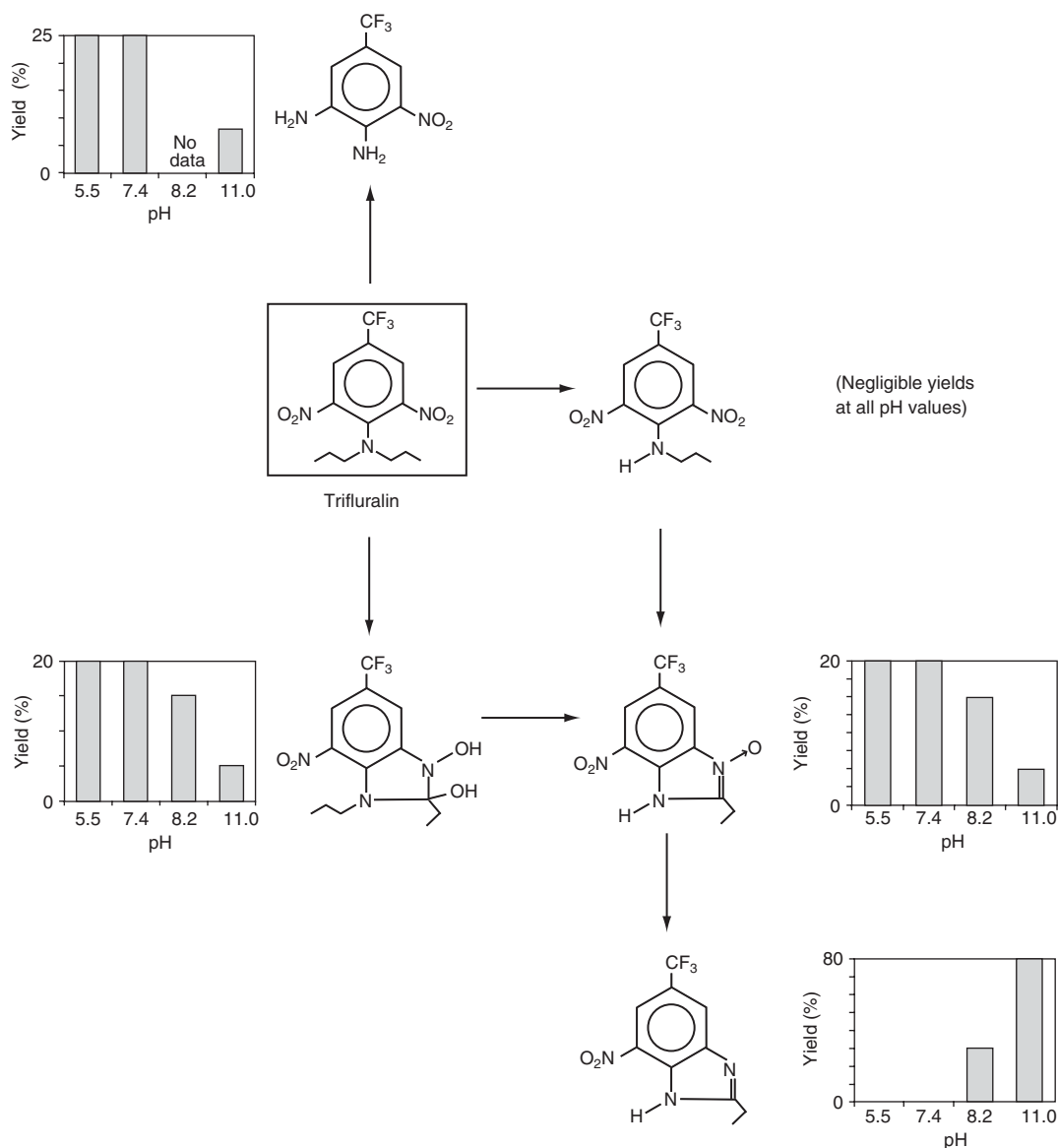


Figure 16 Effects of pH on the yields of different products during the photolysis of trifluralin in summer sunlight (Davis, CA) in water, either with or without soil present. For purposes of display, vertical axis for each product is normalized to the maximum yield for that compound, rather than to 100%. Yields among products at each pH value sum to <100% because data for minor products are not shown. After Crosby and Leitis (1973).

Several authors have combined the Arrhenius equation with kinetic equations reflecting the pH dependence of reaction rates to quantify the simultaneous dependence of pesticide transformation rates on temperature and pH (e.g., Lightfoot *et al.*, 1987; Liqiang *et al.*, 1994; Dinelli *et al.*, 1997). Other work has demonstrated the extent to which E_a values for pesticide hydrolysis vary, if at all, with pH (Lee *et al.*, 1990; Smith and Aubin, 1993; Dinelli *et al.*, 1997, 1998).

Most of what is known about the effects of pH on the rates of pesticide transformation in

aqueous solution has been learned from laboratory studies employing buffers to stabilize pH. However, since they are Brønsted acids and bases, pH buffers may also accelerate these reactions—or cause shifts in the relative rates of different transformation mechanisms—compared with what occurs in unbuffered solution (Li and Felbeck, 1972; Burlinson *et al.*, 1982; Barbash and Reinhard, 1989a, 1992b; Deeley *et al.*, 1991; Smolen and Stone, 1997). Such effects, though, are not observed for all pesticide compounds (Hemmamda *et al.*, 1994; Kochany and Maguire, 1994; Smolen and Stone, 1997;

Hong *et al.*, 2001). Indeed, the absence of buffer effects has been used as evidence for unimolecular reaction mechanisms (Bank and Tyrrell, 1984). The varying tendencies of different buffers to accelerate hydrolysis and dehydrohalogenation are consistent with reactivity trends predicted by the HSAB model (Barbash, 1993) and, for hydrolysis, may be predicted quantitatively using a method introduced by Perdue and Wolfe (1983). Relatively few laboratory studies have accounted for buffer effects (e.g., Li and Felbeck, 1972; Burlinson *et al.*, 1982; Miles and Delfino, 1985; Barbash and Reinhard, 1989a, 1992b; Smolen and Stone, 1997), but failing to make such corrections may lead to overestimates in the rates at which these reactions are likely to occur in natural waters.

Ionic strength. Ionic strength is known to influence some chemical reactions, with both the magnitude of the effect and its direction (i.e., acceleration versus inhibition) depending upon the nature of the reaction in question. The effects of ionic strength on pesticide transformations are of particular interest in saline environments such as coastal waters where pesticides are applied for aquaculture, or estuaries into which significant loads of pesticides are discharged by rivers that drain extensive agricultural (Pereira *et al.*, 1990; Larson *et al.*, 1995; Hainly and Kahn, 1996; Clark and Goolsby, 2000; Lippa and Roberts, 2002; Hladik *et al.*, 2005) and nonagricultural areas (Bondarenko *et al.*, 2004). Transition-state theory predicts that the effects of ionic strength on reaction rates will be smallest for neutral reactants, and become more pronounced with increasing ionic charge on the reactants (Lasaga, 1981). This is consistent with observations regarding the effects of ionic strength on the rates of hydrolysis of pesticide compounds over the range of salinities encountered in most natural waters. As predicted by transition-state theory, these effects have been found to be minor over the pH range (if any) within which a given pesticide compound is subject only (or primarily) to reaction with H₂O (Barbash and Reinhard, 1992b; Liqiang *et al.*, 1994; Bondarenko *et al.*, 2004), but substantial both at higher pH for those compounds that are subject to base catalysis (Miles and Delfino, 1985; Bondarenko *et al.*, 2004) and at lower pH for those subject to acid catalysis (Wei *et al.*, 2000). Also consistent with transition-state theory is the observation by Miles and Delfino (1985) that the effect of salt concentration on the rate of aldicarb sulfone hydrolysis is more pronounced (on a molar basis) for the divalent Ca²⁺ than for the monovalent Na⁺. The effects of ionic strength on photochemical

reactions do not appear to be extensively documented (e.g., Mill and Mabey, 1985), but Walse *et al.* (2004) observed a significant increase in the rate of photolysis of the insecticide fipronil upon the addition of 3% NaCl, suggesting that the rate of this reaction is likely to be higher in marine waters (which typically have salinities of ~3.5%) than in freshwater environments. Ionic strength may also affect pesticide persistence through its influence on the activity of the organisms responsible for biotransformations (Bondarenko *et al.*, 2004).

Concentrations and structure of SAS. SAS that may be present in the hydrologic system—either dissolved in the aqueous phase or as part of the soil—may influence the rates and mechanisms of pesticide transformation. These compounds include fatty acids, polysaccharides, humic substances, and other forms of NOM (Thurman, 1985), as well as the surface-active agents (or “surfactants”) commonly used in detergents or as adjuvants in commercial pesticide formulations. All SAS share the common property of “amphiphilicity,” that is, the ability to associate simultaneously with both polar and nonpolar chemical species in aqueous solution. This property arises from the dual nature of their chemical structure, one portion of the molecule being relatively hydrophilic (and often ionic) and another portion being more hydrophobic. In aqueous solution, these compounds exhibit a tendency to self-associate into assemblages known as “submicellar aggregates” at low concentrations, and “micelles” (Figure 17) above a chemical-specific level (the “critical micelle concentration”). Micelles consist of an inner core comprised of the more hydrophobic portions of the SAS molecules, surrounded by an outer layer comprised of their more hydrophilic portions (Fendler and Fendler, 1975).

When SAS are present in solution, pesticide compounds partition between the bulk aqueous solution and the (sub)micellar phase (Figure 17). This partitioning may affect the overall rates and products of transformation of these compounds if their rates of reaction in the (sub)micellar phase are significantly different from those in the aqueous phase (Barbash, 1987; Macalady and Wolfe, 1987; Barbash and Resek, 1996). In some cases, relatively minor variations in SAS structure can have substantial impacts on pesticide transformation rates (Kamiya *et al.*, 1994). Even if reaction rates are not substantially different in the (sub)micellar phase, however, the presence of SAS may modify reaction rates in solution for sparingly soluble pesticide compounds by simply increasing their dissolved concentrations, as may occur in the presence of polar solvents (e.g., Barbash and Reinhard, 1989a; Schwarzenbach *et al.*,

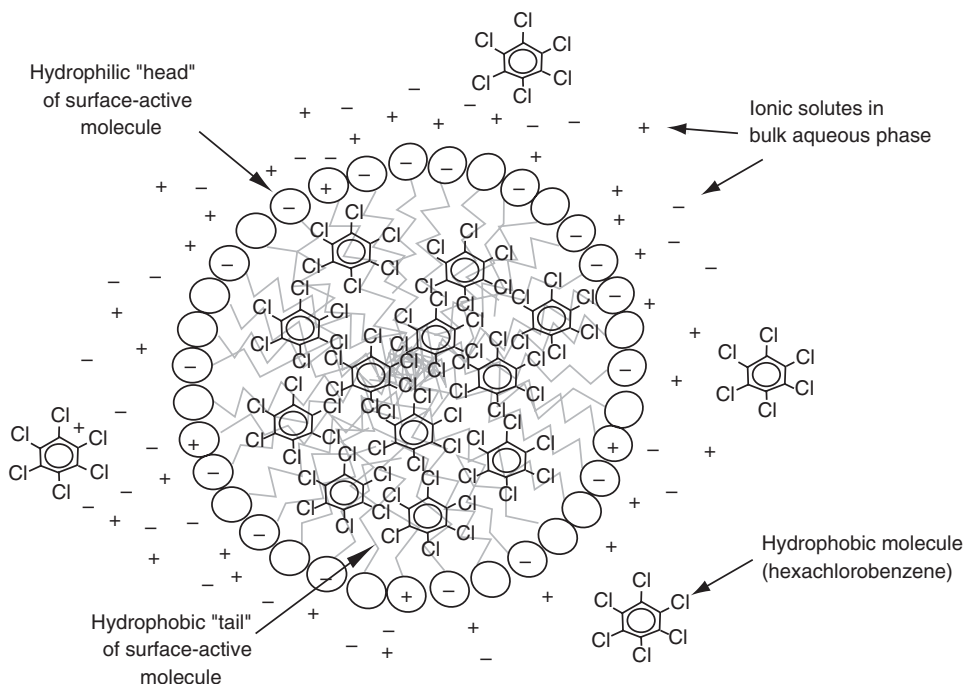


Figure 17 Cross-sectional view of the self-association of surface-active molecules into an idealized micelle. Hydrophobic portion of each surface-active molecule shown as a jagged line and hydrophilic portion shown as a circle. Hydrophobic pesticide molecules, represented by the fungicide hexachlorobenzene, will tend to accumulate within the hydrophobic core of the micelle at a higher concentration than in the bulk aqueous phase. Ionic species (e.g., hydroxide ion) will show the opposite distribution. After [Fendler and Fendler \(1975\)](#).

1993; [Wei et al., 2000](#)). Rates of biotransformation may be either increased or decreased by partitioning into a (sub)micellar phase, depending upon the effect of the particular SAS on bioavailability, and the nature of the microorganisms involved ([Guha and Jaffé, 1996](#)).

The influences of NOM—either in aqueous solution or in the soil phase—on the rates of transformation of pesticide compounds in water are consistent with general principles regarding the effects of SAS on chemical reactions. Because the polar regions of most NOM are either neutral or possess a negative charge, previous research suggests that the presence of NOM in natural waters is likely to accelerate the reactions of pesticide compounds with cations, have a negligible effect on their rates of reaction with neutral species, and inhibit their rates of attack by anions—and that these effects will increase with increasing NOM concentration ([Barbash, 1987](#); [Macalady and Wolfe, 1987](#)). These trends are precisely what has been observed for the transformations of pesticide compounds by acid-catalyzed ([Li and Felbeck, 1972](#); [Khan, 1978](#)), neutral ([Macalady and Wolfe, 1985](#)), and base-catalyzed hydrolysis ([Perdue and Wolfe, 1982](#); [Macalady and Wolfe, 1985](#); [Noblet et al., 1996](#)) in the presence of either dissolved or solid-phase NOM. The

anticipated effects of SAS on the rates of other reactions that may transform pesticide compounds in natural waters (i.e., substitution reactions with other nucleophiles, dehydrohalogenation, reductive dehalogenation, and free-radical transformations) were reviewed by [Barbash \(1987\)](#).

Interfacial effects. The rates and mechanisms of pesticide compound transformation (both biotic and abiotic) at interfaces in the hydrologic system (air/water, water/solid, and solid/air) are often markedly different from those in the adjacent bulk phases (e.g., [Barbash and Resek, 1996](#)). The influence of the air/water interface on these reactions is likely to be most important within the surface microlayer of surface waters, where the more hydrophobic pesticide compounds are likely to concentrate ([Zepp et al., 1975](#))—as alcohols, hydrocarbons, carotenoid pigments, chlorophylls, fatty acids, fatty acid esters, and other naturally derived SAS are known to do ([Parsons and Takahashi, 1973](#)). The gas/solid interface is likely to exert the greatest influence on reactivity at the surfaces of dry soils and plants, or in the atmosphere, where surface-catalyzed reactions of volatile halogenated compounds, including the fumigant methyl bromide, can deplete atmospheric ozone. Among the three principal

types of interfaces in the hydrologic system, however, the solid/liquid interface appears to have received the most attention regarding this topic, and is therefore the main focus of the following discussion.

The presence of natural solids can significantly modify the rates of transformation in aqueous systems—relative to the rates observed in homogeneous solution—for many pesticide compounds, but may have little effect on others (Barbash and Resek, 1996). Factors that can influence the rates and mechanisms of transformation of pesticide compounds at the water/solid interface include the structure of the compound of interest (e.g., Torrents and Stone, 1991; Baldwin *et al.*, 2001), the composition and surface structure of the mineral phase (e.g., Kriegman-King and Reinhard, 1992; Wei *et al.*, 2001; Carlson *et al.*, 2002), the solid-phase organic-carbon content (e.g., Wolfe and Macalady, 1992), and the characteristics, health, and size of the resident microbial community.

Most of the ways in which natural water/solid interfaces influence the rates of transformation of pesticide compounds, however, are consistent with the various effects of related chemical species on these reactions in homogeneous solution, discussed in preceding sections. Russell *et al.* (1968), for example, observed that the hydrolysis of atrazine at low pH was greatly accelerated in suspensions of montmorillonite clay, relative to the rate of reaction in homogeneous solution at the same pH. The authors attributed this effect to the acid catalysis of the reaction by the clay surface, which exhibited a pH that was considerably lower (by as much as 3–4 pH units) than that of the bulk solution. As noted previously, the sorption of pesticide compounds to soil organic matter has been observed to influence the rates of their hydrolysis in the same manner as might be expected from the association of these compounds with SAS in solution, leading to an acceleration of the acid-catalyzed process (Li and Felbeck, 1972), a negligible effect on the neutral process, and an inhibition of the base-catalyzed process (Macalady and Wolfe, 1985).

In addition, several naturally occurring metal oxides exhibit semiconducting properties that may catalyze the photochemical production of hydroxyl and hydroperoxyl radicals in aqueous solution—species that, as noted earlier, can react with pesticide compounds (Zepp and Wolfe, 1987). Chemical structures located at the surfaces of natural solids may also participate in pesticide transformation reactions as Brønsted bases, oxidants (e.g.,

Voudrias and Reinhard, 1986), reductants (e.g., Wolfe *et al.*, 1986), hydrolysis catalysts (Wei *et al.*, 2001), complexing agents (e.g., Torrents and Stone, 1991), or sources of protons for hydrogen bonding (e.g., Armstrong and Chesters, 1968).

Rates of pesticide transformation may be either directly or inversely related to the amount of NOM in the solid phase, depending upon the reaction in question. The common observation of higher transformation rates in more organic-rich soils may result from either enhanced microbial activity in the presence of more abundant NOM (e.g., Veeh *et al.*, 1996) or, in the case of reductive transformations in sterile soils, higher concentrations of biogenic reductants associated with the NOM (Wolfe and Macalady, 1992). By contrast, the inverse relations that have been reported between NOM and pesticide transformation rates are believed to be caused by substantial decreases in the rates of some reactions in the sorbed phase, relative to the dissolved phase (e.g., Graetz *et al.*, 1970; Ogram *et al.*, 1985; Zepp and Wolfe, 1987; Lartiges and Garrigues, 1995; Walse *et al.*, 2002). Indeed, with regard to biotransformations, it is generally assumed that sorption reduces the bioavailability of pesticide compounds (e.g., Zhang *et al.*, 1998). Phototransformations have also been found to occur either faster or more slowly in the sorbed phase, depending upon the substrate structure and the nature of the solid phase (Mill and Mabey, 1985).

9.15.3.5 Effects of Transformations on Environmental Transport and Fate

As might be expected, the transformation of a pesticide can generate products with partitioning characteristics that are substantially different from those of the parent compound. For example, the hydrolysis of 1,3-dichloropropene (Figure 6) and EDB (Weintraub *et al.*, 1986; Syracuse Research Corporation, 1988; USDA/ARS, 1995), as well as the hydration of acrolein (Bowmer and Higgins, 1976), all generate reaction products that are much less volatile—and more water-soluble—than their parent compounds. Similarly, the herbicide chlorthal-dimethyl (dacthal, or DCPA), a relatively hydrophobic dimethyl ester, undergoes transformation in soil to yield progressively more mobile products as it hydrolyzes first to a “half-acid” ester intermediate, and thence to the diacid, tetrachloroterephthalic acid (Ando, 1992; USEPA, 1992; USDA/ARS, 1995). Indeed, one of the principal strategies employed by living

organisms for detoxifying xenobiotic compounds is to convert them—typically through either oxidation or hydrolysis—into products that are more water-soluble, and thus more readily excreted (Coats, 1991).

Neutral reactions do not always lead to an increase in the mobility of pesticide compounds in the hydrologic system, however. For example, for each of several chloroacetamide herbicides, the nucleophilic displacement of chloride by bisulfide has been observed to generate a product that in each case is less water-soluble than the parent compound, with the solubilities of the products decreasing in the same order as those of their parent compounds (Stamper *et al.*, 1997). Atrazine hydrolyzes to form hydroxyatrazine, which is less water-soluble than its parent compound (Erickson and Lee, 1989; Bayless, 2001), and exhibits a nearly 20-fold greater affinity for soil organic matter (based on K_{oc}) than atrazine (Moreau and Mouvet, 1997). An early explanation for the latter phenomenon (Armstrong *et al.*, 1967) suggested that because the replacement of the chlorine atom on atrazine with a hydroxyl group raises the pK_a of the substituted amino groups on the molecule, this also increases its tendency to form hydrogen bonds with soil surfaces.

The oxidation of pesticide compounds usually generates products with aqueous mobilities that are either similar to or greater than that of the parent compound. The oxidation of aldicarb, for example, produces aldicarb sulfoxide and aldicarb sulfone, both of which have lower K_{oc} values than aldicarb (Moye and Miles, 1988). Similarly, because most phototransformations involve either the hydrolysis or oxidation of the parent compound, they yield products that are generally more polar (Mill and Mabey, 1985), and thus more water-soluble than the parent compound. Reduction reactions, by contrast, may result in products that are less water-soluble than their parent compound. Examples include the reduction of aldicarb sulfoxide to aldicarb (Miles and Delfino, 1985; Lightfoot *et al.*, 1987) and the reduction of phorate sulfoxide to phorate (Coats, 1991). The reactivity of transformation products may be either higher or lower than that of their parent compounds. However, those in the former category (i.e., reactive intermediates) are, of course, much less likely to be detected in the hydrologic system than more stable products.

9.15.4 THE FUTURE

Future progress in understanding the geochemistry and biological effects of pesticide

compounds will be fundamentally dependent upon the availability of more detailed information on the temporal and spatial patterns of application and occurrence of these compounds, especially in nonagricultural settings. However, while the spatial and temporal distributions of their sources differ considerably from those of other contaminants, most of the uncertainties that beset our current knowledge of the geochemistry and biological effects of pesticide compounds are essentially identical to those that pertain to industrial solvents, petroleum hydrocarbons, fire-fighting chemicals, personal care products, pharmaceuticals, mining wastes, and the other chemical effluvia of modern life. As with these and other anthropogenic contaminants, predictions regarding the transport, effects, and fate of pesticide compounds in natural waters must take more explicit account of a variety of complex phenomena that have received comparatively limited attention in such assessments to date. These include spray drift, large-scale atmospheric transport, preferential transport in the vadose and saturated zones, nonlinear sorption, time-dependent uptake by soils, endocrine disruption, toxicological interactions among pesticides and other contaminants present in mixtures, the effects of temperature and moisture content on transformation rates, and the transport, fate, and biological effects of transformation products and adjuvants. Until significant progress is achieved in understanding these phenomena and accounting for the magnitude, timing, and spatial distributions of pesticide and adjuvant use and occurrence, the full implications of the ongoing release of these compounds into the Earth's ecosystems will remain unknown.

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