

Environmental Fate of Simazine

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Introduction

This document is a review of the physical properties, transport, fate, and toxicity of simazine (6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine) in the environment (Figure 1). Simazine is an herbicide used to control broad-leaf weeds and annual grasses in crop fields such as fruit orchards. The herbicide is available as a commercial product in powder, liquid, and granular formulations. Simazine has also been registered as an algacide.

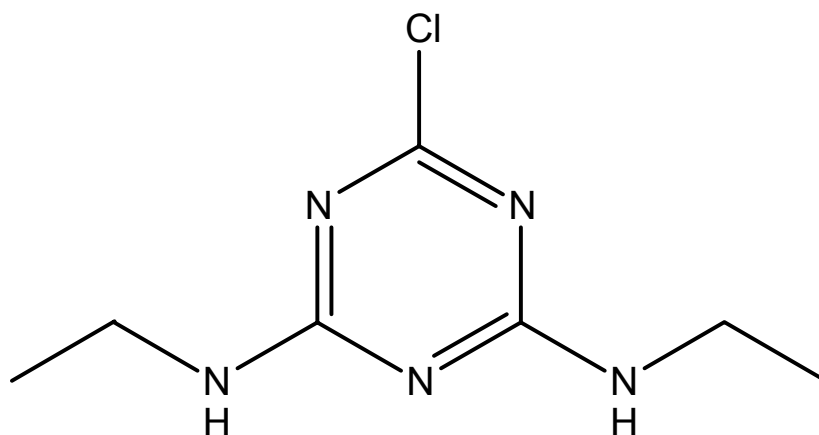


Figure 1. Chemical structure of simazine

History and General Information

Simazine was first introduced in 1956 by the Swiss company J. R. Geigy (Cremlyn, 1990) and is part of the triazine family of chemical compounds (six-member ring containing three carbon and nitrogen atoms). Other chemicals of the triazine family include prometryn and atrazine (Ware, 2000). In addition to the aromatic carbon/nitrogen ring of simazine, it also contains a chlorine and two ethylamine groups attached to the ring (Figure 1). The aromatic nature and stabilization of the carbon/nitrogen ring stems from the electron charge delocalization of the excess electrons between the carbon and nitrogen atoms.

Simazine is the active ingredient in Princep Caliber 90®, Princep Liquid®, and other trade name herbicides as well as in the algicide Aquazine® at active ingredient (a.i.) concentrations of 90%, 42%, and 83%, respectively. Simazine is currently produced by Syngenta. The compound has been heavily used as an herbicide because it is effective at inhibiting the photosynthetic electron transport processes in annual grasses and broad-leaf weeds (Ware, 2000). Wilson et al. (1999) provides a brief, but detailed, explanation

on the mechanisms of photosynthetic electron transport inhibition by simazine. Simazine can be used as a non-selective and selective herbicide at high (5-20 kg/ha) and low (1-4 kg/ha) rates, respectively (Cremllyn, 1990). The compound was also used to control weeds and algae in different water systems prior to 1992. For example, fish farm ponds, aquariums, and cooling towers were some of the many water systems simazine was used in.

Simazine production

Simazine is a colorless to white crystalline solid. It is thermally stable and withstands heating at and above 150°C (Melnikov, 1971). According to Milnikov (1971), simazine (Figure 2 D) can be produced in >90% yield by the reaction of cyanuric chloride (Figure 2 A) with ethylamine (Figure 2 B) and sodium hydroxide (Figure 2 C) in aqueous medium. As an herbicide, it is often marketed as a mixed wettable powder where half of the mixture consists of clay (kaolin) or chalk (calcium carbonate) as diluents (Milnikov, 1971).

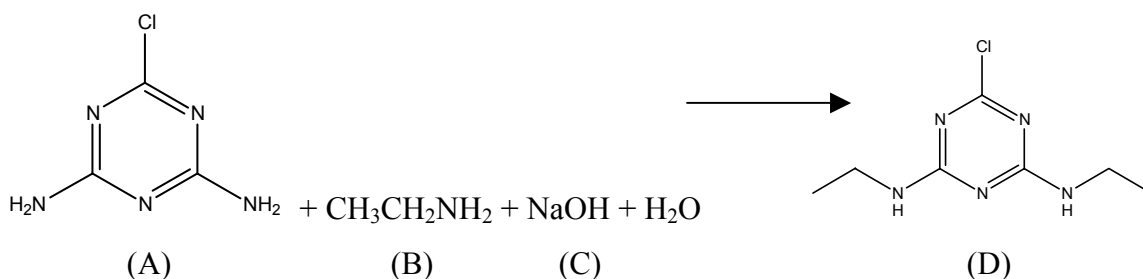


Figure 2. The production of simazine (D) from cyanuric chloride (A), ethylamine (B), and sodium hydroxide (C) in aqueous medium.

Simazine mode of action and byproducts

According to Cremllyn (1990), simazine uptake is via the roots of emerging seedlings. Subsequently, it inhibits the photosynthetic electron transport process in the plant leaves and causes them to turn yellow and die (Ware, 2000). Many varieties of maize and sugar cane plants are resistant to the herbicidal properties of simazine as these plants contain an enzyme that detoxifies the compounds by hydrolysis (Figure 3) in the plant tissues (Cremllyn, 1990).

Simazine can be dechlorinated when the compound is heated with caustic alkalis under laboratory conditions (Melnikov, 1971). In environmental systems, the same dechlorination process and subsequent hydrolysis may take place under high pH conditions (Figure 3). The resulting compound is 2-hydroxy-4,6-bis(ethylamino)-s-triazine (Figure 3 B). Interestingly, this compound does not have herbicidal properties.

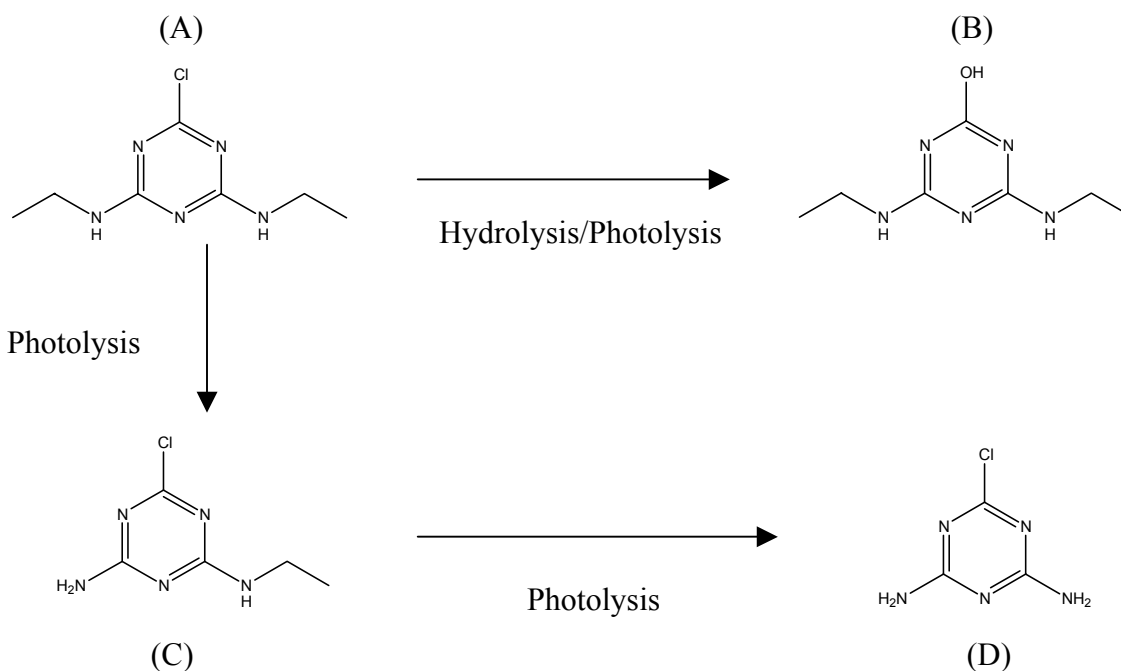


Figure 3. The general degradation pathways of simazine (A) where 2-hydroxy-4,6-bis(ethylamino)-s-triazine (B) is produced by hydrolysis. Photolytic loss of alkyl groups produce deisopropyl atrazine (C) and diamino chlorotriazine (D).

Simazine can also lose an alkyl group and the subsequent product, deisopropyl atrazine (Figure 3 C), was detected in groundwater of the Netherlands by Lagas et al. (1989) and California (Troiano, 2002; Spurlock et al., 2000). Photochemical degradation has been found by Evgenidou and Fytianos (2002) to lead to alkyl group loss and subsequent production of deisopropyl atrazine and diamino chlorotriazine (Figure 3 D).

Abiotic Degradation

Table 1 contains parameters for important physicochemical properties of simazine that affect abiotic degradation, hydrolysis, photolysis, reactivity and remediation, and occurrence in air.

Table 1. Important physicochemical properties of simazine. All parameters are at 25°C, unless specified.

Chemistry Abstracts Service registry number (CAS #) ^a		122-34-9
Molecular formula ^a		C ₇ H ₁₂ ClN ₅
Molecular weight (g/mol) ^a		201.66
Density at 20°C (g/mL) ^a		0.436
Melting point in (°C) ^a		225-227
Octanol-water partition coefficient (K _{ow}) ^a		122
Organic carbon partition coefficient (K _{OC}) ^d		130
Aerobic microbial half life (t _{1/2}) in sandy loam (days) ^a		91
Anaerobic microbial t _{1/2} in sandy loam (days) ^a		70-77
Photolysis t _{1/2} of 6.7 µg/cm ³ at λ = 53.25 nm (days) ^c		4.5
Photolysis t _{1/2} in sandy loam under natural light (days) ^a		21
Henry's Law constant (atm·m ³ /mole) ^a		9.48 x 10 ⁻¹⁰
Acid dissociation constant (pK _a) at 21°C ^c		1.70
Water solubility (mg/L)	0°C ^a	2.0
	20°C ^b	5.0
	22°C ^a	6.2
	85°C ^a	84
Vapor pressure (mm Hg)	10°C ^a	9.0 x 10 ⁻¹⁰
	20°C ^a	6.1 x 10 ⁻⁹
	25°C ^a	2.2 x 10 ⁻⁸
	30°C ^a	3.6 x 10 ⁻⁸
	75°C ^a	4.5 x 10 ⁻⁵
	100°C ^a	9.8 x 10 ⁻⁴

^a Vencill, 2002; ^b Verschueren, 1984; ^c Montgomery, 1993; ^d Average from Wauchope et al., 1992.

Hydrolysis

The effects of hydrolysis on simazine were evaluated by Comber (1999). Comber found that no appreciable degradation of simazine occurred over a period of 100 days at 15°C in the dark at pH 7 and 9. However, a half-life ($t_{1/2}$) of 145 days was calculated for the degradation of simazine at pH 4.0 (lowest pH that would be found in aquatic environments) in the dark indicating that hydrolysis reactions occur at a slow rate.

The hydrolysis of simazine, as influenced by dissolved organic matter (DOM) in natural waters, temperature, and mixing, was examined by Noblet et al. (1996). They found that simazine showed no decrease in concentration in water after 43 days. The presence of 70 mg/L DOM had no catalytic effect on the transformation of simazine at pH 8.0 and 40°C. Noblet et al. (1996) suggest that DOM alone will not influence the transformation of simazine.

The acid-catalyzed hydrolysis of simazine was examined by Sawunyama and Bailey (2002). They calculated the enthalpy of hydrolysis ($\Delta_h H$), Gibbs free energy of hydrolysis ($\Delta_h G$), and entropy of hydrolysis ($\Delta_h S$) at 25°C to be -70, -63, and -23 kJ/mol, respectively. Such a $\Delta_h G$ value indicates the hydrolysis is energetically spontaneous but this was not observed in many studies. Hydrolysis of simazine appears to be kinetically controlled (Sawunyama and Bailey, 2002).

Photolysis

Among the abiotic reactions that may take place in regards to simazine degradation, photochemical reactions play a major role. The photolytic degradation $t_{1/2}$ for simazine ranged from 4.5-21 days (Table 1). Evgenidou and Fytianos (2002) examined the degradation of simazine in natural waters using UV radiation ($\lambda > 290$ nm). They found that in the dark, there was no degradation of simazine in water from three sources (distilled, lake, and river waters). Therefore, hydrolytic processes do not seem to play a significant role in simazine decomposition. Simazine readily degraded in water under UV radiation, however. The $t_{1/2}$ for simazine was calculated to be between 2.7 and 5.4 hours depending on the source of water and other factors such as oxygen content and organic matter (OM) content in the waters. Degradation followed first-order curves. Hydrogen peroxide addition to water significantly enhanced simazine degradation (up to

four times faster degradation). Two degradative pathways are proposed (Figure 3); one involving the dechlorination and subsequent hydroxy substitution of the ring and the other involves the oxidation of the propyl side chains on simazine. The main photochemical degradation products from simazine were found to be 2-hydroxy-4,6-bis(ethylamino)-s-triazine, 2-chloro-4-amino-6-ethylamino)-s-triazine (deisopropyl atrazine), and 2-chloro-4,6-diamino-s-triazine (diamino chlorotriazine).

Further photolysis studies revealed that simazine decomposes in the presence of light ($\lambda < 300$ nm) but the extent of decomposition depended on the type of vessel used. Photolysis of simazine, using artificial light and Pyrex vessels, followed second-order decay, with $t_{1/2}$ for pH 4 and 7 being calculated as 21 and 19 days, respectively. The $t_{1/2}$ in a quartz vessel was 32 days at pH 4. The $t_{1/2}$ increased for simazine in these vessels at higher pH values (pH 7.0). Under daylight conditions ($\lambda = 300$ to 800 nm) the decomposition of simazine at pH 4 was higher than the artificial light results at 6 and 7 days for quartz and Pyrex vessels, respectively. At pH 7, the $t_{1/2}$ in the quartz vessel was 37 days. For surface waters, photolysis can be predicted to occur readily in waters of all pH values; ranging from only about 6 days at pH 4 to between 18 and 37 days at pH 7.0.

Solubility

Table 1 provides the solubility of simazine at four different temperatures. At ambient temperature, 20°C, simazine is moderately soluble (5 mg/L) and its solubility increases with temperature. Curren and King (2001) found that the solubility of simazine increased more than ten fold as the temperature of the water was raised from 50 to 100°C. They observed that at 50 and 100°C, the simazine solubility increased from 17 $\mu\text{g/mL}$ to 240 $\mu\text{g/mL}$ (ppm), respectively.

Reactivity and remediation

Simazine (2.5×10^{-5} M) can be oxidized from ozone (ozonation) by using catalytic amounts of Mn (II) (concentration = 0.1-1 mg/L) and Fe (II) (concentration = 1 to 5 mg/L). The pH was found to be a significant player in the ozonation of simazine using Mn and Fe; an increase of simazine conversion was observed as the pH was raised from 5 to 9. Rivas et al. (2001) found that after 30 minutes reaction time, the conversion of

simazine changed from 80% to more than 90% in the absence and presence (up to 0.2 mg/L) of catalytic amounts of Mn (II), respectively. The main simazine ozonation byproduct detected by means of HPLC was deisopropyl atrazine. Since reactivity of simazine with molecular ozone is low, decomposition of ozone to produce highly reactive species are needed. Thus, small amounts of Mn (II) added to the reaction would facilitate the degradation of simazine. The positive effects of pH (simazine degradation increases with increased pH) can be attributed to the presence of significant amounts of hydroxy ions in solution, which gives way to the non-catalytic decomposition of ozone into free hydroxyl radical ions responsible for simazine degradation. Experimental data by Rivas et al. (2001) indicate that the main route for simazine degradation at high pH is by reaction with “free” hydroxyl radicals arising from the ozone decomposition reaction. The addition of 1.0 mg/L of ferrous iron to Mn led to a slight improvement of the simazine degradation (Rivas et al., 2001). However, the use of these metals at higher concentrations led to reduce simazine degradation.

Simazine may be effectively removed from water using the photo-assisted Fenton reaction. Huston and Pignatello (1999) found that simazine degraded to 99.8% and 100% of the initial concentration (0.342×10^{-4} M) after 10 and 30 minutes, respectively, when subjected to a system with the following conditions; 0.00005 M Fe(III), 0.01 M H₂O₂, pH of 2.8, temperature of 25°C, and 1.2×10^{19} quanta/L/s of fluorescent backlight UV irradiation (300-400 nm). The photo-Fenton reaction is optimum at pH 2.8 when half of the Fe(III) is present as Fe³⁺ and half as Fe(OH)² ion, the ion active species.

Occurrence in Air

The potential for simazine to volatilize from a soil and water system is low as observed by the compounds low vapor pressure and Henry’s constant shown in Table 1. The vertical fluxes of simazine were measured by air-sampling and aerodynamic measurement, over 24 days, after surface application of the compound on a fallow soil by Glotfelty et al. (1989). Calculated volatilization losses of simazine in the first 21 days were 0.021 kg/ha of 1.68 kg of a.i./ha (1.3% loss). Daily losses depended on moisture content because simazine, applied as a wettable powder, became susceptible to wind erosion as the soil surface dried in the noontime solar radiation. However, the

volatilization losses were much smaller than dissipation by chemical degradation but equivalent to reported surface runoff concentrations (Wauchope, 1978).

Biotic degradation

The aerobic and anaerobic degradation half-life values in Table 1 indicate that simazine is persistent in the environment (up to eight months) and not easily degraded by microbes. However, biotic degradation seems to be the most effective method of simazine degradation compared to the abiotic processes. Strong and coworkers (2002) have found a gram-positive bacterium, *Arthrobacter aurescens* strain TC1, that is capable of consuming 3000 mg/L of atrazine in liquid as a sole carbon and nitrogen source via catabolism to supplement its growth. This bacterium is also capable of degrading 23 other s-triazines, including simazine. Similarly, Martin-Montalvo et al. (1997) found a bacterium strain (DSZ1) capable of growing solely on simazine as a carbon and nitrogen source. The growth of the organisms in the presence of simazine takes place with a lag phase. Significant bacterial growth was observed at 5, 10, and 20 mg/L simazine. The optimum conditions at 10^6 cells/mL were 5 mg/L simazine where 70% of the initial simazine concentration was degraded in 19 days. A lag phase of six days was observed at this concentration. The study found that DSZ1 could grow at low simazine concentrations as well (2 mg/L). Cook and Hutter (1984) found that *Rhodococcus corallinus* was capable of transforming deethyl-simazine (a byproduct of simazine) by dehalogenation, dealkylation, and hydroxylation, but the bacterium could not cleave the triazine ring. Kodama et al. (2001) found a bacterial strain (N5C) identified as *Moraxella ovis* that is capable of degrading 200 mg/L simazine, completely (100%), within 5 days. These bacteria grow well at high pH but pH values around 5 are suitable for simazine degradation by this strain.

In addition to bacterium capable of degrading simazine, fungal strains have been identified as well. Kodama et al. (2001) found that fungal strain, DS6F (*Penicillium steckii*) gradually degraded 50 mg/L of simazine in a 25 mg/L yeast extract. The fungal strain can grow with simazine as its sole carbon and nitrogen source but grows better with small amounts of yeast extract. The rate of simazine degradation was improved when easily accessible carbon sources were added into the medium (the reduction rate of

53% simazine was obtained after 5 days of cultivation at 30 °C when glucose was added to the medium). *Phanerochaete chrysosporium*, a popular white rot fungus poorly degraded ¹⁴C labeled simazine (5.4%) into deisopropylatrazine as found by Mougín et al. (1997). Analysis of the white rot fungus primary mode of macro-organic matter degradation, extracellular lignin peroxidases and manganese-dependent peroxidases to carry out the N-dealkylation of simazine proved unsuccessful (Mougín et al., 1994).

From a molecular and mechanistic perspective, the effect of microbial enzymes (phenol oxidases such as laccases or peroxidases) on the potential to oxidize simazine via oxidative coupling reactions has been explored by Sannino et al. (1999a). In this particular study, a laccase (benzenediol), a well-characterized enzyme, isolated and purified from *Cerrena unicolor* was used as an oxidative catalyst. The presence of simazine in the reaction mixture often resulted in the inhibition of laccase activity. Such results are supported by Filazzola et al. (1999) where they showed that simazine behaves as an inhibitor of laccase-mediated-catechol transformation. Laccase has been shown to be a positive oxidative substance that can efficiently transform toxic substances such as catechol (Filazzola et al., 1999).

Environmental Fate of Simazine

Soil

A major concern with any agricultural pesticide is its potential to leach from the soil to surface or ground water systems that are used as drinking water sources. The sorption and desorption of simazine in soils play a fundamental role in the prevention of contamination of water, which in turn is affected by the heterogeneous nature of soil systems having different soil types and amounts of organic matter (OM). A number of literature reports have used a variety of soils to study the sorption behavior of simazine. Simazine retention and sorption in soils will be discussed using literature reports in relation to the 1. mineral fraction of soil, 2. organic matter content, 3. soil moisture content, and 4. influence of agriculture practices.

1. Sorption to minerals

A study on simazine sorption onto hydroxyl aluminum coated and uncoated montmorillonite (hydrated silicate hydroxide containing sodium, calcium, aluminum, and magnesium) was conducted by Sannino et al. (1999b). Simazine was adsorbed more to clays at low pH (3.7) and uncoated clay surfaces ($K_{oc} = 458$) (Table 2), whereas, simazine sorption to hydroxyl aluminum coated montmorillonite was reduced ($K_{oc} = 16$). The sorption curves of simazine in this study showed two types of sorption; a fast one followed by a slow one. Such sorption behavior indicated the presence of diffusion-controlled processes. Desorption experiments showed that very little simazine was desorbed from the montmorillonite clay surface indicating strong electrostatic interactions (low concentration of simazine). In a similar study by Celis et al. (1997), it is reported that montmorillonite is the main mineral soil colloid contributing to simazine sorption and in contrast, ferrihydrite, an iron oxide mineral, does not sorb simazine. They also reported that when hydrophobic processes are not dominant, interactions and competition for sorption sites between simazine and water molecules can take place (Laird et al., 1992).

Table 2. Summary of simazine sorption to different sorbates.

Author	%OC	Sorbent	Conditions	K_D (ml/g)	K_{oc}	Method
Sannino et al., 1999b	0	Montmorillonite	pH = 3.7	458	458	Isotherm
			pH = 5.6	16	16	Isotherm
			pH = 3.7 and Al(OH) _x = 18 mequiv Al/g clay	19	59	Isotherm
Beltran et al., 1998	0.1	Soil with different % OC		0.4	400	Breakthrough curves
	3			25	833	
Brereton et al., 1999	NA	Black fly silk		19000		Isotherm
Reddy et al., 1992	0.5	Fine sand		0.29	58	Isotherm
	1.39	Fine sandy loam		1.06	76	
Barriuso et al., 1997	1.08	Soil		0.78	74	Breakthrough curves
	16.87	Compost		10.5	62	
Cox et al., 1999	0.66	Soil			67	Isotherm
	2.53				44	
Cox et al., 2000b	0.66	Sandy soil		2.9	445	Isotherm
	~16	Sandy soil with solid OOMW ⁺⁺ amendment		16	1550	
	0.76	Montmorillonite		12.9	1700	
	~16	Montmorillonite with solid OOMW ⁺⁺ amendment		21.5	1537	

⁺ Freundlich adsorption parameters

⁺⁺ Organic olive-mill waste

The sorption of simazine to six, mineral rich, Brazilian soils was studied by Oliveira et al. (2001). The soils were composed of goethite and gibbsite, hematite, and 1:1 clays such as kaolinite, with low OM content. Simazine sorption to these soils did not correlate to silt or sand content. The K_{oc} for simazine in the soils were low at less than 116. Other studies have reported similar low K_{oc} values; 103-152 (Ahrens, 1994), 105 (Hassink et al., 1994), and 130 (Flury, 1996). Oliveira et al. (2001) found that simazine would leach from mineral rich, OM poor soils. The connection between simazine release and mineral rich soils has also been explored by Cox et al. (2000a) who found that the sorption of simazine was very low in sandy-clay soil (20% clay, 10% silt, and 70% sand). Subsequent desorption of simazine from the soil was fast (no hysteresis) indicating the compound will readily leach into water systems from sandy soils. The study also found that simazine could sorb to hydrophobic micro-sites, located between the charge sites, on low surface charge montmorillonite surfaces; greater opening in the silicate layer allows for enhanced interlayer sorption. These studies indicate that the mineral components of soil can absorb simazine to a low extent but lack the retaining capacity for the herbicide.

2. Sorption to organic matter

The partitioning of simazine to organic compartments such as octanol and OM (Table 1) is not very significant (K_{ow} and $K_{oc} \sim 125$) in comparison to chemicals having a strong affinity for soil such as dichlorodiphenyl-trichloroethane (DDT); DDT K_{oc} ($\sim 160,000$) and K_{ow} values are orders of magnitude greater than simazine. A number of notable studies have been conducted to understand the impact of OM on simazine sorption and desorption. For instance, Beltran et al. (1998) studied the adsorption and desorption of simazine using sandy Western Australian soils (Table 2). They found the primary mode of adsorption and desorption are controlled mainly by diffusion and a correlation was found between increased simazine retention and greater OM content. However, the K_{oc} values (833 with 6% OM) are still relatively low in terms of overall simazine sorption when compared to other more hydrophobic compounds such as DDT. Flow, at the rate of 3 meters/day through the soils containing simazine, resulted in a lack of equilibrium as observed by reduced K_D values (40 to 60%) compared to a static system; indicating slow equilibrium processes and thus, lower sorption affinity. This

study indicated that in mineral rich, OM poor soil systems, leaching of simazine could be significant. Reddy et al. (1992) also shows that simazine could have a tendency to leach from sandy soil systems that lack significant amounts of OM. Their study examined the percent sorption of simazine in sandy soils having 1 and 2.8% OM. With increasing OM content, simazine sorption increased significantly; from 19 to 46% sorption for the 0.5 and 1.39% OC containing sandy soils, respectively (Table 2).

Other studies have focused on understanding the molecular level binding properties between simazine and OM. Celis et al. (1997) found that desorption of simazine from OM fractions such as humic acid was lower than montmorillonite and stems from the OM sorption affinity for simazine. The affinity of OM to sorb simazine is presented in a corresponding study by Celis et al. (1998). They found that when soil minerals (ferrihydrite and montmorillonite) are in association with OM fractions, such as humic acid, the sorption capacity for simazine greatly increased. The main bonding mechanism in hydrophobic environments between simazine and OM (humic substances) was determined to be hydrogen bonding and proton transfer processes. It is important to note that although the simazine sorption affinity described here is greater than the sorption affinity for the mineral fraction of soil it is significantly lower than the overall sorption affinity of other more hydrophobic pesticides such as DDT.

Barriuso et al. (1997) examined the sorption of simazine to OM rich materials such as compost and compared the results to simazine sorption in OM poor soils. Simazine sorption to compost ($K_D = 10.5$ L/kg) was approximately 13 times higher than in soil ($K_D = 0.78$ L/kg) and was attributed to the greater OM content in compost (16% greater for compost than soil). They found that the amount of simazine extracted was reduced with increased OM content and degradation of the compound was similar to atrazine; triazine ring mineralization. However, on a K_{oc} basis, no significant difference in the sorption materials could be observed (Table 2).

Laabs et al. (2002) used ^{14}C labeled simazine to understand the degradability and bound residue formation in an organic matter rich (Ustox) and poor (Psamments) tropical soil. Simazine persisted more in the organic rich Ustox. The 50% dissipation time (DT_{50}) of simazine, added at a concentration of 2 kg/ha, was longer in the organic matter rich soil; 27 days in Ustox and 14 days in the sandy Psamments soil. They found that between

55-60% of the applied simazine was non-extractable. The effects of OM sorption and retention of simazine was further analyzed by Cox et al. (2001) who found that different organic amendments had a direct influence on simazine leaching potential. For example, they found that organic amendments to a mineral soil greatly enhanced simazine sorption. The main mechanism of sorption was predicated to be a partitioning mechanism and other reports (reported here) support such a hypothesis. Solid organic amendments to the mineral soils resulted in the greatest sorption increase; a factor of 2.5 compared to the non-amended soil. The liquid form of OM is predicted to contain dissolved OM that competes with simazine molecules for sorption sites on minerals such as montmorillonite. The binding of ^{14}C labeled simazine to compost was also investigated by Ertunc et al. (2002) who found that simazine binding to compost was fast; aqueous extractions after 29 and 200 days of composting (equivalent to the thermophilic and mesophilic phase of composting) produced only 4.2 and 3.1% simazine, respectively. Such data coincides well with the nature of the compost materials, which become more recalcitrant with time and obtain a greater sorption affinity for organic contaminants. The non-extractable fraction of simazine was greater (64%) after 29 days of composting. A distinct shift from rather weak interactions to strong covalent linkages to simazine and its major metabolites with increasing composting time was observed.

A significant sorptive component of OM is dissolved organic matter (DOM). DOM is defined as the fraction of OM that can pass through a 0.45 μm filter membrane. Hartlieb et al. (2001) investigated the distribution of simazine in compost DOM. They found that simazine was mainly associated with the low molecular DOM fraction (60% simazine associated with <1 kDa fraction) up to 200 days composting. However, from 200 to 370 days of composting, simazine was associated with the large DOM fraction (50% associated with >100 kDa fraction). They also found that 16% of the initial concentration of simazine (1.17 mg/kg) was mineralized at the 370-day period of composting. After 370 days, 65% of the initial concentration was non-extractable and bound to the compost matrix. Although low molecular weight fractions of OM can act as a major sorbent for simazine, Matsui et al. (2002) has shown that it can also compete with simazine for sorption sites on high affinity water remediation materials such as activated carbon. Using micro-column experiments, Matsui et al. (2002) observed that low

molecular weight molecules competed directly with strongly sorbing pesticides such as simazine for adsorption sites (7-12 Å width micropores) on activated carbon. Cox et al. (1999) found that simazine sorption to soil (K_F) can be increased by a factor of 2.5 and 1.8 with 20% w/w and 10% w/w of a 26% liquid organic amendment to a sandy (75%) soil, respectively. Desorption studies found that at the high concentrations of simazine is reversible but at low concentrations it is not, as indicated by increased hysteresis (Cox et al, 1999). Likewise, Cox et al. (2000b) found that in a sandy soil, a good sorbent for simazine was solid well-humified organic olive-mill waste; the simazine isotherm sorption capacity was higher in the organic amended soil as compared to the soil alone (Table 2). They also found DOM, produced as a result of a liquid organic amendment, will compete with simazine molecules for sorption sites on montmorillonite and increase the potential for simazine to leach from the soil; simazine sorption to the organic amended montmorillonite had approximately the same K_{oc} as the non-amended montmorillonite (Table 2).

In an attempt to make practical these findings, Davis and Lydy (2002) conducted a three-year simazine runoff study at a golf course. They found rainfall events on a golf course caused simazine runoff at high concentration in two centrally located ponds after the spring and summer applications. A significant decrease in the macroinvertebrate diversity and population size was also observed. However, upon the incorporation of buffer zones around the ponds (establishment of aquatic vegetation, and rerouting of drainage systems to a maintained filtration area, based on the principals of best management practice) they found a significant reduction, and in some instances, elimination, of simazine in the two ponds. They also observed complete recovery of the diversity and population size in the macro-invertebrates in the ponds.

Similar to golf course buffers on ponds, riverbed sediments act as buffers to river flow. Daniels et al. (1998) found that the sorption of simazine onto the sediment significantly influences the rate of penetration of the compound. They found that sediments with greater surface area and organic carbon content had more affinity (larger K_D) for simazine. Also, simazine concentrations decrease with increasing depth of the soil and greater depths being achieved as a function of time. For instance, concentrations of 10 µg/kg simazine penetrated ~30 mm in 7 days. After 37 days, the same

concentration had penetrated ~60 mm. Finally, low concentrations of simazine reached the 89 mm depth, the maximum depth of the soil in this particular experiment. The study found that sorption significantly influences the rate of simazine diffusion.

Snails and small insects provide another significant contribution to the overall OM content in soils. Simazine sorption to byproducts of these animals could be significant when considering the overall sorption processes in the environment. Brereton et al. (1999) examined the sorption of simazine to snail pedal mucus and blackfly silk and found that sorption of simazine to these materials were orders of magnitude greater than for soil. The K_D of simazine to blackfly silk was 19000 while for soil it was 135 (Table 2). Given the high density of such organic material near rivers and streams, the potential for simazine to be sorbed and enter the food chain is significant. This study showed that simazine could enter the food web through pathways other than soil and water systems.

3. Soil Moisture

Soil moisture has been shown in many studies to contribute to the sorption and dissipation of simazine. Wang et al. (1996) found the $t_{1/2}$ of simazine to be 34 days under 20% field capacity. A relationship was shown to exist between the temperature and residue of herbicides in soil and also a positive tendency was observed between soil moisture content and degradation; higher temperature and moisture content lead to faster degradation of simazine. The effect of moisture content on the sorption and degradation of simazine was further explored by Garcia-Valcarcel and Tadeo (1999). They examined the effects of 4-18% moisture content on the degradation rate of simazine in a sandy loam soil and found sorption capacities (K_F) of 0.9, 0.848, and 1.215 (averages) corresponded to 10, 18, and 4-18% soil moisture content. A partitioning mechanism was supported in this study given the linearity of the isotherms (Freundlich exponent $N=1$). More interesting was that soils subjected to the wetting and drying cycles had the highest simazine sorption values (K_F values ranged from 0.5-1.2 for simazine), which corresponded to the shrinkage and swelling of the soil matrix; resulting in a decrease of soil surface area which may enhance the diffusion of the pesticide into the soil matrix. The simazine $t_{1/2}$ was calculated to be between 27 and 126 days and depended on the soil moisture content between 4-18%. This study also found that increased simazine sorption

was observed for aged residues incubated at various soil moisture contents. Soil moisture field studies were initiated by Louchart et al. (2001) who examined the effects of wet and dry soil conditions on the degradation of simazine in southern France. They found that two phases governed the decrease of simazine in the surface soil layer (0-2 cm). The first phase decrease of simazine was fast and attributed to soil moisture conditions, which were high and led to increased microbial activity. The second phase showed that the decay of simazine was slow due mainly to dry conditions and decreased microbial activity (part of the Mediterranean climate). Therefore, the dry conditions led to the prevalence of substantial amounts of simazine.

4. Influence of Agriculture Management Practices

Farming practices can play a major role on determining if simazine releases to water systems. Several studies have examined the importance of agricultural practices on simazine loss. Louchart et al. (2001) compared simazine runoff in no-till versus tilled fields in southern France where a Mediterranean climate prevails. The tilled fields had lower runoff simazine concentration due to increased infiltration capacity. In agreement, Lennartz et al. (1997) report that in fields that had not been tilled, there was no vertical simazine transport below the soil (18, 55, and 26% clay, silt and sand, respectively) depth of 2 cm under the same Mediterranean climate as described in the study by Louchart et al. (2001). In the tilled sites, Lennartz et al. (1997), found simazine extending to depths of 15 cm in a soil (22, 48, and 29% clay, silt, and sand, respectively). These agricultural practices have a profound effect on the dissipation kinetics of simazine. For instance, Lennartz et al. (1997) determined that no-till fields had a shorter dissipation time (DT) than tilled fields; 85 for the DT_{50} and 281.5 days for the DT_{90} in no-till fields whereas in the tilled fields the DT_{50} and DT_{90} were 157 and 523 days, respectively (DT_{50} and DT_{90} are when 50 and 90% of the simazine is dissipated, respectively). The findings clearly show that tillage appeared to reduce the rate of simazine dissipation. Such findings are further supported by Glenn and Angle (1987). They found that no-till fields would greatly increase the runoff of pesticides. Glenn and Angle (1987) found that conventional tillage reduced simazine runoff by 70% as compared with no till corn plots. Often in orchards, the area between the trees, are not tilled at all. Since simazine is extensively used in

orchards, runoff of the herbicide into surface waters following application could be high. Troiano and Garretson (1998) examined the movement of simazine in runoff water from citrus orchard row middles (area between furrows without tree growth) as affected by mechanical incorporation and runoff events. In the first simulated rainfall event (540 L corresponding to 32 mm of rainfall water) in the undisturbed row middles, the simazine mass concentration in the runoff water was 179 ± 40 mg/plot from the 4120 ± 300 mg/plot simazine applied (about 4% runoff). Simazine runoff from the second simulated rainfall event, applied one week after the first event, was reduced by more than half (1.6% simazine runoff). Mechanical incorporation of the row middles drastically reduced simazine runoff concentrations as well. For instance, simazine runoff was reduced by an order of magnitude (ten times) after mechanical incorporation as determined in the first runoff event by comparing the undisturbed and mechanically incorporated row middles. This study clearly shows that simazine applied to orchard row middles with compacted (non-tilled) soils are a significant factor contributing to the simazine concentration in runoff water from rainfall events. Mechanical incorporation of these areas could notably reduce simazine runoff.

The leaching potential of simazine from nursery plots was tested in field conditions by Stearman and Wells (1997). Red maple nursery plots having 5% slope was treated with simazine from fall to the following spring and tilled. Simazine was detected at depths of 60-90 cm after the first rainfall event. Approximately, 0.1-6.8% simazine applied to the plots was exported in runoff water. Significant (>3 $\mu\text{g/L}$) concentrations of simazine were observed in the water from the runoff events. The study showed that simazine is persistent in the soil and was present in the top 20 cm although some simazine moved deeper into the soil profile. A recent report (Revitt et al., 2002) that monitored urban runoff of simazine over two years found concentrations of simazine between 0.1 and 0.45 $\mu\text{g/L}$, which resulted from rainfall events. Although, not greater than the maximum contaminant limit (MCL), such research shows that in the absence of OM and sorption media for simazine, a significant amount of the herbicide can accumulate in water bodies from urban rainfall events.

Liu and O'Connell (2002) have examined the effect of rotor sprinklers on simazine loss in runoff water. They evaluated the runoff system by the application of 2 kg

a.i./ha without and with irrigation in a California citrus orchard. Simulated runoff events with 3.5 cm of water revealed that the non-irrigated area had the largest simazine runoff (6.5% of the initial treatment). Thus, herbicide runoff is greatly enhanced in compacted, low permeable soils by rainfall events. In a subsequent study (2003), Liu and O'Connell have shown that the current applied rate of 2 kg a.i./ha can be reduced to 1 kg a.i./ha. The reduced rate, applied by spraying, achieved the same amount of weed control as did the higher 2 kg a.i./ha in an orchard floor. The study confirms that reduced use of simazine resulted in significantly lower mass losses of the herbicide in runoff water without affecting the compounds herbicidal properties.

In contrast to the above findings, the correlation between tillage and groundwater contamination by simazine was examined by Ritter et al. (1996) who reported finding a maximum simazine concentration higher in the groundwater under tillage conditions than no-tillage. Simazine concentrations on the tilled plots ranged from <0.10 to 16 ug/L and <0.10 to 6 ug/L at the 3 and 4.5 m depths, respectively. Their most significant finding was that pesticides might move to shallow groundwater by macro-pore flow in sandy soils of the mid Atlantic states if more than 30 mm of rainfall occurs shortly after application. Further studies on the long-term simazine movement through soil with low water tables (<3 m) was examined by Cogger et al. (1998) in western Washington. Simazine was applied for three years to a raspberry field with sandy/silt loam (recent alluvium) soils at a rate of 4.5 kg/ha annually. At this application rate, simazine was found to degrade slowly, persisted with time, and increased in overall concentration over the sampling period. Soil and water analysis showed that most of the simazine was retained in the top 15 cm (between 400 and 2310 ug/kg) of the soil but small amounts (from trace amounts to 15 ug/kg) moved further into the soil profile (120-180 cm depth). Simazine $t_{1/2}$ were found to be 175 and 424 days for the first and second years of application, respectively, and remained in the soil up to four years after application. Mean annual precipitation was 1035 mm from autumn and winter rains. Simazine concentrations in well water samples were related to rainfall. This study found that preferential flow (short-circuiting of water and solute through soil macro-pores during periods of heavy rainfall or irrigation) and non-equilibrium sorption and desorption (time

dependent and slow sorption compared to transport and degradation) drive simazine leaching and thus, the herbicide will continue to leach after application is ceased.

In addition to a reduction in simazine use, reductions of simazine runoff to water systems can be initiated with cover crops. For example, Stearman et al. (1997) found that cover crops such as rye grass and crimson clover significantly reduced the runoff concentration of simazine as compared to plots without a cover crop (runoff from clean till plots were as much as 6.8% of applied rate).

Water

Simazine as a contaminant in water systems is of primary importance because ground and surface waters are used in many communities as the primary source of drinking water. Simazine, and its degradation products (deisopropyl atrazine and diamino chlorotriazine), have been extensively monitored in California. Table 3 is a summary of the presence of simazine in California surface and well waters. The table shows that simazine reaches both surface and ground waters and in some cases approaches the U. S. MCL of 4 µg/L (Table 4).

Table 3. The presence of simazine in surface and ground water in California in µg/L.

Parameter	Surface water			Ground water		
	2000	2001	2002	2001	2002	2003
Year	2000	2001	2002	2001	2002	2003
Total number of sites	221	460	147	1019	1173	2347
Number of detections	36	166	4	3	87	17
Maximum Concentration	2.892	3.700	0.156	0.252	0.244	0.103
Minimum Concentration	0.050	0.011	0.050	0.193	0.034	0.050
Median Concentration	0.160	0.024	0.068	0.223	0.104	0.098

Data from California Department of Pesticide Regulation Surface and Ground Water Databases, 2004.

Table 4. Water Quality Criteria in µg/L.

U. S. EPA MCL (maximum contaminant level) ^g	4
U. S. EPA MCLG (maximum contaminant level goals) ^g	4
North Carolina Ground Water Quality Standard (1998) ^h	3.5

^g U.S. EPA, 2003; ^h Wade et al., 1998.

Simazine detections in environmental water systems have been reported in 1. groundwater wells, 2. rivers and surface waters, 3. estuaries, and 4. rainfall.

1. Groundwater wells

Spurlock et al. (2000) examined the distribution of simazine and its byproducts, deisopropyl atrazine (Figure 3 C) and diamino chlorotriazine (Figure 3 D), in 18 domestic water wells in Fresno and Tulare counties, California. The byproducts significantly contributed to the overall triazine concentration in groundwater (24 to 100%) and accounted for the greatest fraction in the wells. In the 30 wells sampled, at least one triazine and simazine reached a high concentration of 3.8 µg/L (95% of the U.S. MCL). A correlation was found between simazine concentration and the concentrations of the byproducts, indicating that wells with high simazine concentrations also had high byproduct concentrations. The overall herbicide concentrations did not change over the two years sampled. Similar results were found in a study conducted by Troiano (2002). He found that of 131 wells with detections, 110 wells had deisopropyl atrazine (Figure 3 C) and 105 wells had diamino chlorotriazine (Figure 3 D), both simazine breakdown products, but only 85 wells had the parent compound, simazine. The study further found that simazine was a significant source of the breakdown products and the combined concentration of the breakdown products was greater than the parent compound, simazine. In North Carolina, a comprehensive study of 97 groundwater wells found simazine at concentrations that were 9 to 34% of the North Carolina ground water quality standard (3.5 µg/L) in three wells, 57% in one well, and 211% in one well (Wade et al., 1998). Further reports revealed that simazine was found in 89 of 1430 groundwater wells throughout the U.S. (Holden et al., 1992), 56 wells in Illinois (Long, 1989), and 10 of 20 wells in Wisconsin (Habecker, 1989).

International localities have also been affected by the global use of simazine. For instance, in Denmark, simazine in concentrations <0.1 µg/L was found in two shallow groundwater wells of 35 sampling locations in a clay dominant soil area (Spliid and Koppen, 1998). The study also reported that in the sandy soil areas, 12 of 184 shallow groundwater wells were contaminated with simazine but at low concentrations (below 0.1 µg/L).

2. Rivers and Surface Water

Battagline and Goolsby (1999) investigated the presence of simazine in surface waters as related to application time, in agricultural areas of the U.S. They found that in Midwestern U.S. rivers elevated concentration of simazine occurred during runoff events from 1-3 months following the seasonal application of simazine. The presence of simazine was evaluated in 53 Midwestern rivers during the first major runoff events after herbicide application in 1989, 1990, 1994, and 1995. The most common observation was that simazine occurrence was greatest in waters following its application and became reduced in the months following application. For example, Albanis et al. (1998) found simazine concentrations as high as 0.317 $\mu\text{g/L}$ in groundwater from May to August and these concentrations diminished significantly during the autumn and winter months. Similarly in Paris (France) Chevreuil et al. (1996) found simazine concentrations in the atmosphere reached maximum values after the local agricultural herbicide use in the spring (June and July of 1993). A recent report (Revitt et al., 2002) that monitored urban runoff of simazine over two years found runoff concentrations between 0.1 and 0.45 $\mu\text{g/L}$ and was directly related to rainfall events. Although, not greater than the MCL, this study showed that simazine can accumulate in water bodies from urban rainfall runoff events following the seasonal application of simazine. Louchart et al. (2001) found that the first runoff event, in a simulated runoff field-experiment, resulted in the greatest loss of simazine from the soil (580 $\mu\text{g/L}$ on no-till field); more than 68% of annual loads of simazine were observed during the first runoff event. Watershed outlet monitoring of the experimental site revealed that the simazine concentration decreased proportional to the runoff concentrations in the fields; more than 94% of simazine was removed from the fields by only four storm events corresponding to less than 10% of the annual runoff volume in the Mediterranean climate of southern France. As explained before in this report, Louchart et al. (2001) found that tillage substantially reduced herbicide losses as compared to no-till fields. Lennartz et al. (1997) also found that most of the pesticide runoff coincided with the high initial rainfall events under the same climate as described by Louchart et al. (2001); the first runoff events after applications exhibited, in general, the largest measured concentration of herbicide runoff. At the no till site, seasonal simazine losses were 1.25% of the applied amount (1 kg/ha) while the tilled plots had a

simazine loss of 0.79%. The first rainfall event after application resulted in >87% of the seasonal simazine losses and therefore, simazine loss depended on runoff volume and intensity. Stearman et al. (1997), who examined the runoff of simazine in nursery plots, found that most of the simazine runoff was associated with the first runoff event and the intensity and duration of the rainfall event were important variables in determining herbicide runoff as was the proximity of the time of the chemical application (less runoff in spring as less rain, compared to fall).

Runoff events carry simazine to rivers and large water bodies where the compound can undergo transformational changes due to abiotic and biotic processes. Vink and van der Zee (1997) have studied the transformation of simazine under anaerobic conditions. They approached this study by examining the simazine transformation and sorption in undisturbed soil and lake sediments. Simazine showed some reductive transformation with decreasing oxygen concentration (over 200 days). The transformation of simazine (>90%) in aerobic and anoxic soil columns was approximately 22 and 53 days, respectively. However, in anaerobic lake sediment, more than 30% of the initial concentration simazine (4.5 µg/g) remained after 200 days of incubation. The possible transformations of simazine under reduced conditions are provided in Figure 3.

The transformation of pesticides in surface waters was also studied by Vink and van der Zee (1997). The $t_{1/2}$ of simazine was found to be 1 to 139 days. Principal component analysis (PCA) revealed the discriminating environmental variable that determined the transformation rate of simazine was reduced to three underlying components that explained 84% of the total variance in the data. The first component contained variables that promote biorespiratory processes, in which a relationship existed between sorption potential, N nutrient sources, and microbial activity. The second component is the macro/micronutrient group and the third component is the phosphorus group. The incubation showed that at 100 mg/L a.i. simazine there was no lag phase in the transformation pathways; first order transformation. The results showed a 30% reduction of simazine concentrations after 3 weeks of incubations.

The reduction of simazine usage over time was investigated by Power et al. (1999). They found statistically significant improvements in water quality from 1988 to

1997. Time was a significant variable in the statistical analysis and accounted for 55.2% of the variation in simazine concentration. They found that there was approximately a 91% reduction in simazine concentrations in the Thames Estuary from 1988 to 1997. Although no specific reasons for the reduction in simazine concentration were given by Power et al. (1999), Battagline and Goolsby (1999) found that improved agricultural practices (split herbicide applications, decreased per acre application rates, increased use of post emergence herbicides, and utilization of herbicide best management practices) have reduced the presence of simazine leaching over time in Midwestern rivers; less simazine concentration was found in 1994-95 compared to 1989-90.

3. Estuaries

Simazine concentration has been measured in estuaries that eventually receive river water carrying runoff water. One estuary that receives high amounts of pesticide runoff applied upstream is the Chesapeake Bay estuarine drainage area. For instance, the usage rate of simazine in the Patuxent River watershed (230 ha) that drains into the Chesapeake Bay estuary was 1600 kg a.i. in 1996 (Harman-Fetcho et al., 1999). Harman-Fetcho et al. (1999) found simazine concentrations as high as 0.8 ug/L in the estuary. The average upstream (Patuxent River) simazine concentration was 0.55 ug/L while downstream it was 0.04 ug/L. These simazine concentrations indicate intense local usage near the upstream area of the Patuxent River, which eventually drains into the Chesapeake Bay. A similar study by Power et al. (1999) found that in the river Thames estuary (England), simazine concentrations peaked in June (0.12 and 0.167 ug/L in 1988 and 1997, respectively) and declined in autumn. This trend clearly showed that simazine loss from agricultural application is greatest following the herbicides application and will move downstream over time to estuaries.

4. Rainfall

The concentrations of simazine in rainfall were low compared to surface and groundwater contamination. Albanis et al. (1998) found a simazine concentration of 0.005 ug/L in rainfall in the Imathia plains of Greece. Studying the fallout of simazine in Paris, France, Chevreuil et al. (1996) found concentrations between 5 to 650 ng/L.

Inferring that pesticides have the potential to contaminate the air and thus be present in precipitation, Dorfler and Scheunert (1997) compiled data from already published studies showing that concentrations of simazine were highest between the time of s-triazine herbicide application. The findings of simazine in non-agricultural area precipitation (unpolluted regions) supports the conclusion that simazine can be rapidly transported over far distances in the atmosphere. For example of the collected precipitation data, the highest simazine concentrations close to the source was 8.1 µg/L while remote from the source it was 0.088 µg/L. Shertzer et al. (1998) found low concentrations of simazine (0.15 µg/L) in rainwater near the Conodoguinet Creek watershed in south central Pennsylvania in 1991.

Plant and microbial toxicity

The general toxicity data has been summarized in Tables 5 through 8. Algae are sensitive to simazine in concentrations at or below the U.S. MCL (4 µg/L) whereas fish and higher order animal are more tolerant to the compound.

Table 5. Simazine Toxicity to Algae

Species	Test	Concentration (µg/L)
Chlorococcum ^e	50% decrease in growth	2.5
Dunaliella tertiolecta ^e	50% decrease in growth	4.0
Isochrysis galbana ^e	50% decrease in growth	0.6
Phaeodactylum tricornutum ^e	50% decrease in growth	0.5

Table 6. Simazine Toxicity to Fish and Aquatic Life

Species	Test (LC ₅₀)	Concentration (mg/L)
Daphnia Magna ^f	48-hr	1
Oysters ^a	96-hr	>3.7
Bluegill sunfish ^b	48-hr	130
Bluegill sunfish ^f	96-hr	>100
Rainbow trout ^f	96-hr	2.8
Fathead Minnow ^f	96-hr	6.4

Table 7. Simazine Toxicity to Mammals

Mammal	Test	Concentration (mg/kg)
Rat ^a	Inhalation 4-hr LC ₅₀	5.5 mg/L
Rat ^f	LD ₅₀	>5000
Rabbit ^a	Dermal LD ₅₀	3100

Table 8. Simazine Toxicity to Other Animals (Wildlife)

Animal	Test	Concentration (mg/kg)
Bobwhite quail ^a	LD ₅₀	1785
Bobwhite quail ^f	LC ₅₀ (8 day)	11,000
Mallard duck ^a	LD ₅₀	>10,000
Mallard duck ^f	LC ₅₀ (8 day)	>5000
Mallard duck ^f	Reproductive NOEC*	150
Earthworm ^a	LC ₅₀ in soil	>1000

* No-observed effect concentration. ^a Vencill, 2002; ^b Verschueren, 1984; ^c Walsh, 1972; ^f Extoxnet, 2003.

The toxicity tests in tables 5 through 8, deal primarily with the direct toxicity (i.e., LD₅₀) for algae and higher order animals. The indirect toxicity of simazine that occurs through the interaction of plants, soil, and biotic compartments cannot be examined through direct toxicity techniques. Numerous studies have attempted to study this indirect toxicity of simazine. For instance, Mason and colleagues (2003) hypothesized that since simazine is a well-known photosynthetic inhibitor of submerged and emergent weeds, high concentrations of simazine may be stressing salt marsh plant communities and hence accelerate erosion in Britain; as plant stress increases and growth decreases, the plants are less capable of withstanding tidal forces. Wilson et al. (1999) found that the accumulation of simazine into *Canna hybrida* or 'Yellow King Humber', a perennial ornamental plant, could be positively correlated with the cumulative water uptake by the plants root system. They found that fresh weight of *Canna hybrida* was reduced 85 and 89% at 1 and 3 mg/L simazine, respectively, after a seven-day exposure. Observable symptoms of chlorosis appeared after 5 days with necrotic lesions occurring shortly thereafter. The compound accumulated primarily in the leaves of the plants with some accumulation in the roots. No

accumulation was found in the tubers or stems. In a subsequent study by the same group (Knuteson et al., 2002), they found that more mature, older plants of the same species were more tolerant to simazine than younger plants.

The indirect toxicity of simazine was also investigated in the laboratory by Mason et al. (2003). They focused on the production of benthic diatom biofilms, which contribute to sediment stability through the production of extracellular polymeric substances (EPS). Simazine concentrations as low as 33.7 nM had a significant inhibitory effect on diatom growth. The inhibition of diatoms by simazine and the lack of EPS production were hypothesized to lead to the destabilization of salt march plant communities and increased soil erosion. Further, the diatoms migrated further down into the soil profile upon the addition of simazine to the top few cm of the soil. Effects on the photosynthetic capability in both diatoms and higher plants was significantly decreased at 168 nM simazine, an herbicide concentration found in freshwater habitats. Decreased cell numbers and EPS content shows that there was a statistically significant decrease in sediment stability as a result of plant death by simazine toxicity. In contrast to these findings is a study that found that microbes in soil can tolerate simazine concentrations up to 30 times more than normally used in agriculture (300 µg/g) without evident modifications to their growth (Martinez-Toledo et al., 1996). They added five different concentrations of simazine, ranging from 10 to 300 µg/g, to soil to determine the toxicity of the herbicide to aerobic bacterial populations, fungi, aerobic denitrogen-fixing bacteria, denitrifying bacteria, and nitrogenase activity. The results showed that the bacterial populations described were not affected at any concentrations after 30 days of incubation at 20°C, except for the nitrifying bacterial population, which decreased at the 50 µg/g simazine concentration and above. The two studies differed in relation to the medium and the way simazine was applied. The study by Mason et al. (2003) measured effects in organisms living in submerged anaerobic soil whereas Martinez-Toledo et al. (1996) measured effects on aerobic microbes in surface soil.

Summary

Although the direct toxicity of simazine in terms of LD₅₀'s in higher order organisms is low, Mason et al. (2003) have shown that simazine can have significant indirect effects through multi-mechanistic environmental process. For instance, the toxicity to diatom population's lead to reduced EPS, which can then destabilize the soil and plant communities. However, at high simazine concentrations, Martinez-Toledo et al. (1996) found that in soil, some microbes can resist the compounds toxicity. Such apparent toxicity differences in water and soil can be observed when comparing Tables 6 and 7 where aquatic higher order organisms are more susceptible to concentrations of simazine than non-aquatic organisms. Even though the solubility of simazine in water is low (6.2 mg/L), organisms in water may have greater exposure than organisms in soil because OM in soil may sorb simazine and prevent the compound's release. Further, water suspended DOM may also limit the exposure of microbes and higher order organisms, such as fish, given simazine's low but important affinity to organic constituents. Simazine in stable submerged soils has been found to sorb beyond the top few mm of the soil. Yet, given these sorptive materials in soil, Brereton et al. (1999) has shown that blackfly silk and snail pedal mucus to have sorption affinities for simazine that are orders of magnitude greater than soil. The correlation between greater sorption capacity of simazine with increased soil moisture and temperature was confirmed (Wang et al., 1996). Garcia-Valcarcel and Tadeo (1999) extrapolated the results by Wang et al. (1996) to find that the lack of soil moisture resulted in decreased microbial activity and thus persistence of simazine in soils during dry conditions.

The physical conditions prevailing in farmed soil has been shown to have an effect on simazine transport and dissipation. For instance Louchart et al. (2001) and Lennartz et al. (1997) have found that tilled fields lower simazine runoff. Such findings are important to surface water contamination when considering that in mature orchards where simazine is applied in significant concentrations, no annual soil tillage may take place. Rainfall events promote the transport of simazine into surface waters as found in the nursery plot study with simulated rainfall (Stearman and Wells, 1997). In contrast Ritter et al. (1996) found that tillage of soil will lead to the contamination of simazine in shallow groundwater wells with more than 30-mm rainfall. Increased rainfall and

groundwater well contamination was confirmed by Cogger et al. (1998) under field conditions and that preferential flow and non-equilibrium sorption and desorption of simazine in soil were the main driving forces. The use of cover crops such as rye grass and crimson clover can be used to reduce the runoff of simazine to surface waters (Stearman et al., 1997).

The effects of tillage on preventing simazine runoff can be attributed to biotic constituents of the soil that enhance its degradation. For instance, Strong et al. (2002) found a bacterium capable of consuming simazine as its sole carbon and nitrogen source. Other studies have isolated bacteria species (Martin-Montalvo et al., 1997; Kodama et al., 2001) and fungi (Kodama et al., 2001; Mougin et al. 1997) that are capable of degrading simazine at concentrations that are orders of magnitude greater than its MCL of 4 µg/L.

The presence of simazine in water systems has been widely reported, e.g., Spurlock et al. (2000) found simazine and its byproducts in concentrations close to the U.S. MCL in domestic water wells in central California. Further studies by Holden et al. (1992), Long (1989), and Hebecher (1989) found simazine was present in a number of groundwater wells in North Carolina, Illinois, and Wisconsin, respectively.

Simazine runoff and presence in surface and groundwater was related to the seasonal application of the chemical. For instance Albanis et al. (1998) and Chevreuil et al. (1996) found that high simazine concentrations were found in groundwater from May to August, after seasonal application, and diminished significantly during the autumn and winter months. Another important factor contributing to simazine runoff is rainfall events. Louchart et al. (2001) found that the first simulated runoff event resulted in the greatest loss of simazine as confirmed by Lennartz et al. and Stearman et al. in 1997. Vink and van der Zee (1997) found that once simazine reaches soils within water bodies (anaerobic conditions) the degree of simazine degradation can decrease. The transformation of simazine in surface water was between 1 to 139 days and depended on the sorption potential, N nutrient sources, and microbial activity (Vink and van der Zee, 1997). Rain water has been found to contain simazine (Albanis et al., 1998; Dorfler and Scheunert, 1997). The studies found that the concentration of simazine in precipitation can be directly related to time of application where the concentrations are highest immediately following application and decrease over time. Power et al. (1999), and

Battagline and Goolsby (1999) confirmed that regulated management practices over time have a direct effect on the reduction of simazine concentrations in water bodies.

The process for reducing the persistence and subsequent breakdown of simazine in soil and water systems is its abiotic decomposition. Excluding the properties of DOM sorption and retention of simazine, Noblet et al. (1996) found that DOM will not hydrolyze simazine. Photolysis has been shown to degrade simazine. The $t_{1/2}$ of simazine was calculated to be a matter of hours in relation to the photolytic breakdown of simazine and pH has a kinetic effect (shorter degradation time at low pH) according to Evgenidou and Fytianos (2002). Other important abiotic parameters are temperature and solubility. Temperature enhances the solubility of simazine in water (Curren and King 2001). A number of abiotic reactions involving Mn and Fe have also been found by Rivas et al. (2001) and Huston and Pignatello (1999). These processes can be incorporated into the remediation process of simazine from waters; photo-assisted Fenton reaction (Huston and Pignatello, 1999). The partitioning of simazine to air does not seem to be significant but the herbicide is susceptible to wind erosion after application (Wauchope, 1978).

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