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ATRAZINE, SIMAZINE, AND CYANAZINE(Shaughey II)
080807A. STRUCTURAL SIMILARITIES AND DIFFERENCES

Atrazine, simazine, and cyanazine share the following structural similarities;

- a. All of them contain a 1,3,5- triazine ring (that is, a symmetrical triazine ring).
- b. All of them contain a chloro group (-Cl group) attached to the carbon-6 (C-6) position.
- c. All of them contain substituted amino groups attached to the C-2 and C-4 positions.
- d. All of them contain an ethyl substituent on the amino group attached to the C-4 position.

The structural difference between atrazine, simazine, and cyanazine lies on the type of substituent on the amino group attached to the C-2 position. These substituents are as follows: 1. An isopropyl group in atrazine; 2. an ethyl group in simazine; 3. a methylpropanenitrile group in cyanazine. The reactivity of these herbicides is expected to be influenced by the steric and/or electronic interactions arising from the different substituent groups. However, a discussion of these interactions and how they influence reactivity is beyond the scope of this review (See structures in Figure 1 of Appendix).

B. DEGRADATES

Three types of degradates are possible for atrazine and simazine. The first type of degradate is formed via dealkylation of the amino groups, for which mono- and fully dealkylated degradates are known. The second type of degradates is formed by substitution of a chloro group by a hydroxy group in either parent or dealkylated degradates. The third group incorporates a hydroxy group to a substituent in an amino group. The latter type of degradate has been found predominantly with simazine, but always in extremely low quantities (<1%).

As it will be shown later, the reactivity of the nitrile group plays a major role in the degradation of cyanazine, resulting in the transformation of the original methylpropanenitrile group to a methylalanine group via methylpropamide. Replacement of the chloro substituent by a hydroxy one with and without de-ethylation also occurs, but always accompanied by transformation of the nitrile group. A degradate in which the methylpropanenitrile group has been removed has been identified, but only in very minor amounts.

The registrants of atrazine and simazine (Ciba-Geigy) and of cyanazine (Shell/du Pont) have assigned the following codes to the major degradates:

G-34048 "Hydroxy Atrazine": 2-ethylamino-4-hydroxy-6-isopropylamino-
s-triazine

- G-30414 "Hydroxy Simazine": 2-hydroxy-4,6-bis(ethylamino)-s-triazine
- G-28273 2,4-Diamino-6-chloro-s-triazine
fully dealkylated atrazine/simazine
"des-ethylated and des-isopropylated atrazine"
"bis(des-ethylated) simazine"
- G-28279 2-Amino-4-chloro-6-ethylamino-s-triazine
"des-isopropylated atrazine"
"mono-desethylated simazine"
DW-4002, Degradate form from cyanazine by removal of the
methylpropanenitrile group.
- G-30033 2-Amino-4-chloro-6-isopropylamino-s-triazine
"des-ethylated atrazine"
- SD-20258 2-([4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino)-2-methylpropamide
- SD-20196 N-[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]-2-methylalanine
- SD-20262 2-[(4-chloro-6-amino-1,3,5-triazin-2-yl)amino]-2-methylpropane-nitrile
- SD-31223 N-[4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine

Note that G-28273 and G-28279 are degradates common to both atrazine and simazine; G-28279 (DW-4002) is a common degradate for atrazine, simazine, and cyanazine. Structures of degradates are presented in Figures 2 and 3 of the Appendix.

C. ENVIRONMENTAL FATE DATA

Results from environmental fate data reviewed by EFGWB for these three herbicides are presented below in a comparative manner. The results cited here come solely from studies submitted by the registrants. Only acceptable or supplemental studies have been used in the comparison. Second Round Reviews for atrazine and simazine were completed on 11/18/88 and 7/11/89, respectively. Cyanazine is a List A chemical undergoing review; the in-depth review for this chemical was completed on 8/8/90.

I. Physical/Chemical Properties Relevant to Environmental Fate and Transport

	ATRAZINE	Simazine	Cyanazine
Solubility in Water (ppm)	30 (20 C)	3.5 (20 C)	171 (20 C)
Vapor Pressure (torr)	3.0×10^{-7}	6.1×10^{-9}	1.0×10^{-8}
Henry's Law Constant ($\text{atm} \cdot \text{m}^3 \cdot \text{mol}^{-1}$)	2.58×10^{-9}	3.2×10^{-10}	3.17×10^{-12}
Octanol/Water Partition Coefficient ($\log K_{ow}$)	2.68	2.51	2.24

II. Laboratory Degradation Studies

1. Hydrolysis

pH 5

pH 7

pH 9

ATRAZINE

———— No changes observed over a 30-day period ————

Simazine

———— No changes observed over a 30-day period ————

Cyanazine

$t_{1/2}$ = 148 days -No changes observed over a 30-day period.

Comment: The major degradate identified for cyanazine was N-[4-(ethylamino)-6-hydroxy-1,3,5-triazin-yl]-2-methylalanine. The amount of this degradate increased with time and reached 13.5% of the applied dosage at the completion of the study (30-days). Note that in the formation of this degradate, reaction of the nitrile group to a carboxylic acid group occurs together with elimination of the -Cl group followed by hydroxylation. Hydrolysis is not a rapid degradation process for atrazine, simazine, or cyanazine.

2. Photodegradation Studies

a. In Water

In the presence of chemical sensitizers there is evidence that atrazine may degrade to some extent via indirect photolysis; however data are insufficient to fully access the effect of sunlight on the degradation of atrazine. This also appears to be the case for simazine.

In pH 7 buffer, cyanazine photodegraded under natural sunlight with with a half-life of 43 days. About 30% of the degradate 2-[(4-chloro-6-amino-1,3,5-triazin-2-yl)-amino]-2-methylpropanenitrile was present after 30 days irradiation; under dark conditions ca. 99% of parent cyanazine remained unchanged after 30 days.

b. On Soil

For atrazine and simazine there are also evidences that the presence of natural photosensitizers in the soil may contribute to their degradation, but the quality of the studies does not allow a full assessment of the importance of indirect photolysis in the degradation of atrazine and simazine. From acceptable data, it is known that cyanazine is prone to photodegradation (half-life of 6-days in Hanford sandy loam soil). The major degradates in treated soils samples exposed to natural sunlight were N-[4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine and 2-[(4-chloro-6-amino-1,3,5-triazin-2-yl)amino]-2-methylpropanenitrile ("des-ethylcyanazine") at 10% and ca. 4% of the applied dosage after 10 days, respectively.

Comment: The contribution of photolytic processes to the degradation of atrazine and simazine is unclear at this point; additional

information and/or new studies have been requested under the Data Call-In for these herbicides. Note that photoreactivity may provide a significant degradation route for cyanazine.

3. Metabolism Studies

a. Aerobic conditions

For both atrazine and simazine, there are data indicating that microorganisms can contribute to their degradation in soils. However, the calculated half-lives are greater than 100 days, indicating that these herbicides are still somewhat persistent in soils. Dealkylated and "hydroxy atrazine/simazine" degradates have been identified (see "Degradates" section). The calculated half-lives for atrazine and simazine were 146 days (loam soil) and 110 days (silt soil), respectively. After one-year incubation, most of the applied dosage in both cases was associated with bound residues (ca. 50%). For simazine, the degradate found in highest amount was "mono-deethylated simazine" (G-28279) at ca. 10% maximum of the applied after 60 days, but for atrazine this degradate did not exceed 2% at any time. "De-ethylated atrazine" (G-30033) formation increased with time, but did not exceed 5%.

Unlike atrazine and simazine, cyanazine is less persistent in soils. The reported half-life of cyanazine was found to be ca. 17 days in a Hanford sandy loam soil. The initial degradate detected at >10% was 2-([chloro-6-ethylamino)-1,3,5-triazin-2-yl]amino)-2-methylpropamide (after 7 days; then reached a maximum of ca. 30% after 30 days). This degradate lead to the formation N-[chloro-6-(ethylamino)-1,3,5-triazin-2-yl]-2-methylalanine (36% maximum after 90 days). In turn this latter degradate underwent further transformation to N-[4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine (31% maximum after 1-year). Other two minor products (<7% after 1-year posttreatment) were the des-ethylated-chloro- and hydroxy-1,3,5-triazine-2-yl)-2-methylalanine.

Data on the biodegradation of simazine under aerobic aquatic conditions (required to support its aquatic uses) are not adequate at the present time. However, the mono-deethylated degradate was detected in ca. 10% maximum after application. The hydroxy analogue of this degradate was also detected but always at less than 5% of the applied. No data on the kinetics of degradation are available.

Comment: Note that again in the degradative pathway of cyanazine, reactions of the nitrile group (first to the propamide and then to a carboxylic acid group) plays a significant role. Des-ethylation can occur in conjunction with reactions of the nitrile group. For the three herbicides considered here, mineralization or formation of volatile products are not important biodegradative pathways.

b. Anaerobic Conditions

Both atrazine and simazine in sandy clay sediments under anaerobic aquatic conditions degraded extremely slow (half-lives ca. 660 days). In the case of atrazine, the des-isopropylated and des-ethylated degradates and "hydroxy atrazine" were found at 1.4%, 4.7%, and 5% of the applied dosage, respectively, after 1-year posttreatment. For simazine the mono-desethylated and the fully dealkylated degradates were found at ca. 7% and 0.6% of the applied dosage after 1-year posttreatment while "hydroxy simazine" was found at ca. 7%. After 1-year period the total amount of atrazine and simazine remaining was predominantly associated with the aqueous phase (ca. 70% of the applied dosage for both atrazine and simazine).

Cyanazine, on the other hand, degraded with a calculated half-life of ca. 108 days in Hanford sandy loam soil flooded after a 17-day aerobic incubation period and maintained anaerobic for 60 days. At the time of flooding, the amounts of parent cyanazine, 2-[[4-chloro-6-ethylamino)-1,3,5-triazin-2-yl]amino-2-methylpropamide, N-[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]-2-methylalanine, and N[4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine were 53.4%, 26%, 4.8%, 7.8%, respectively; after completion of the anaerobic incubation, the remaining amounts were 36.4%, 23%, 7.9%, and 14.6%, respectively.

Comment: Note that for atrazine, simazine, and cyanazine the rate of microbial degradation decreases when anaerobic conditions are reached.

III. Laboratory Mobility Studies

1. In Soils

There are acceptable data on Freundlich constants for atrazine, simazine and their major degradates in four different soils (Sequatchie sandy loam, Sassafras sand, and Sharkey clay from Maryland and Hesperia loam from California).

Freundlich adsorption constants (K_{ads}) for parent atrazine ranged from 0.20 to 2.45 (K_{oc} s from 38 to 155); for simazine, K_{ads} s ranged from 0.65 to 4.31 (K_{oc} s from 103 to 152). Adsorption of atrazine and of simazine was the strongest on clay soil. Atrazine adsorbed the weakest on sand, but simazine adsorbed the weakest on loam soil.

The common dealkylated degradates G-28273 and G-28279 adsorbed, in general, slightly weaker than parent atrazine or simazine. The K_{ads} s for G-28273 (the fully dealkylated atrazine or simazine) ranged from 0.16 to 1.56 (K_{oc} s from 31 to 76). The K_{ads} s for the degradate G-28279 ("des-isopropylated atrazine" "mono-deethylated simazine") ranged from 0.6 to 2.73 (K_{oc} s from 30 to 96). The de-ethylated degradate of atrazine (G-30033) adsorbed even weaker (K_{ads} s 0.06 to 1.10; K_{oc} s from 12 to 44) than parent or the other two dealkylated degradates.

On the other hand, both "hydroxy atrazine" and "hydroxy simazine" were stronger adsorbed than either parent or the dealkylated degradates. The K_{ads} for "hydroxy atrazine" ranged from 1.98 to 389.6 (K_{oc} s 374-13797) and for "hydroxy simazine" from 8.48 to 483 (K_{oc} s 1600-17100). For both degradates adsorption was the strongest on clay soil and weakest on sand soil.

While parent atrazine or simazine and their dealkylated degradates are expected to be rather mobile, the hydroxy analogues of atrazine or simazine are expected to be the least mobile. Tables I and II in the Appendix summarize the data obtained from the batch-equilibrium adsorption/desorption studies conducted with atrazine, simazine and their major degradates. In general, there was some correlation between strength of adsorption and percent of organic matter content of the soil.

Data for the mobility of cyanazine and its degradates comes from soil thin layer chromatography (TLC) studies. Data showed that parent cyanazine was mobile in sandy loam, silty clay loam, and loam soils (R_f 0.49-0.55) and very mobile in silt loam soil (R_f 0.75). The degradates 2-([4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino-2-methylpropamide, and N-[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]-2-methylalanine were very mobile in all of the soils (R_f 0.65-1.00). The degradate N-[4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine was mobile in sandy loam soil and very mobile in the other soils. The soils used in the study were Hanford sandy loam, Catlin silty clay loam, Walla Walla silt loam, and Webster loam.

2. Volatility from Soil

Vapor pressure values of below 10^{-6} Torr at 20 C, suggest that atrazine, simazine, and cyanazine would not be expected to volatilize from soils. The low Henry's Law constants also indicate a low tendency for these herbicides to be transported by volatilization.

IV. Field Dissipation Studies

1. Terrestrial

Although multiple many terrestrial field dissipation studies have been and reviewed for both atrazine and simazine, none of the studies have been deemed fully acceptable. However, there are data indicating that the dissipation half-lives of atrazine may range from 60 to 120 days in sandy loam soils. For simazine, half-lives from 44 to 231 days have been reported in a variety of soils and climates. There are no terrestrial field dissipation data currently available on cyanazine.

2. Aquatic

Only simazine has aquatic uses. The available data indicate that the half-life of simazine in swimming pools and man-made ponds range from 7 to 14 days.

D. CONCLUSIONS

Available environmental fate data indicate that atrazine and simazine are likely to be more persistent in water and in soils than cyanazine. All of these three parent herbicides have been found to be rather mobile in a variety of soils. Even though cyanazine may be less persistent, there is still a high probability for cyanazine (as well as for atrazine and simazine) to leach to ground water and/or be transported to surface waters by dissolved run-off, particularly during heavy rainfalls. This concern also extends to the degradates of cyanazine and the dealkylated degradates of atrazine and simazine. The hydroxy analogues of atrazine and simazine would be expected to be, in general, less mobile than parent or the dealkylated degradates. However, there is evidence that in soils with a high sand content the hydroxy analogues may be also mobile.

Studies have shown that when conditions change from aerobic to anaerobic the rates of parent degradation decrease. This has important consequences. When water containing atrazine, simazine or cyanazine moves downwards through the soil profile, the persistence of these herbicides is expected to increase as the concentration of oxygen decreases. Persistence in ground water and in poorly aerated or anoxic surface waters, where the oxygen levels are very low, is also expected to be higher than in well-aerated waters.