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The Dietary Exposure Branch has prepared this dietary exposure analysis in order to estimate the average residues of the herbicide, atrazine, to which the human population is likely to be exposed through dietary routes. These residue estimates will then be used in calculating dietary exposure and chronic risk by the Tolerance Assessment System (TAS).

Atrazine is a selective herbicide (non-selective when used at highest registered rates) used to control weeds in numerous crops including corn, guava, Macadamia nuts, pineapples, sorghum, sugarcane, wheat, grass and proso millet. Tolerances are established ranging from 0.02 (N) ppm in milk to 15 ppm in grasses (40 CFR 180.220).

Three formulations of atrazine are registered for application to crops, Aatrex[R] 4L (4 lbs.a.i./gallon emulsifiable concentrate, EPA Reg. No. 100-497), Aatrex[R] 80W (80% a.i. wettable powder, EPA Reg No. 100-439), and Aatrex[R] Nine-0 (90% a.i. water-dispersible granules, EPA Reg. No. 100-585).

The Atrazine Registration Standard was issued on 9/30/83 (Residue Chemistry Chapter, 7/11/83). In response to the Standard, Ciba-Geigy submitted 63 volumes of residue chemistry (or related) data (MRID Nos. 404313-26, -45 to -83; 404314-01, -14, -18, -20 to -33, -36 to -40; 404375-02). Included were metabolism studies (cattle, poultry, goats, rats, sheep, sorghum, corn), analytical methods, storage stability data, field trial data (corn, sorghum, wheat, proso millet, macadamia nuts), and feeding studies (poultry and cattle). We have reviewed the volumes of these data which were applicable to this dietary exposure assessment (see Bibliography) in order to obtain the information necessary for the dietary exposure assessment only. These data will be more thoroughly reviewed as part of the Second Round Review (SRR) of the Atrazine Registration Standard.

Additional data reviewed as part of this dietary exposure assessment include several published articles on atrazine metabolism, and information submitted with several tolerance petitions (PP#7F0620, PP#0E2398, PP#3F2772/FAP3H5371, PP#4F1425, PP#3F2870).

<u>Summary</u>

The total toxic residue (TTR) for atrazine on plants and animals includes parent atrazine, its N-deethylated metabolite (G-30033), its N-deisopropylated metabolite (G-28279), and the N,N-didealkylated metabolite (G-28273)(see chemical names and structures in Table 2 under Detailed Considerations). Residue data for all of these metabolites are available for all commodities for which atrazine is registered except for guava and pineapples. For these 2 commodities, residue data are available only for parent.

Average residues for all raw and processed commodities (including animal feed items) to which atrazine may be applied are summarized in Table 1. These average values should be used in the Tolerance Assessment System (TAS) risk and dietary exposure assessment since atrazine has chronic (rather than acute) toxic effects. These estimates were arrived at based on data from two sources: residue field trials and FDA Surveillance Monitoring Data. Residue field trial data for each commodity are examined in detail later in this review.

The FDA Surveillance Monitoring Program monitors residues in all raw agricultural commodities and many processed commodities and animal feeds on which atrazine residues are likely to be found. Atrazine is partially recovered by PAM I, 212.1, and is recovered and quantifiable using the Luke method and a nitrogen-selective detector with a limit of detection of approximately 0.05 ppm. In a telecon with FDA (M. Metzger, DEB, with Ellis Gunderson, FDA, 7/29/88), it was reported that less than 10 detectable findings of atrazine have been reported since 1978 (none prior to 1978). FDA monitors greater than 2000 samples each year using analytical methods capable of determining atrazine residues. However, FDA monitors residues of parent atrazine only, not metabolites. As discussed, metabolites may make up a large portion of the total residue, particularly at long PHI's. Therefore, the FDA data is of limited usefulness in assessing total residues likely to be

found in these commodities; and for the purposes of this dietary exposure assessment, FDA data were used only in a qualitative way to support the low residues of parent found on many commodities which FDA analyzes routinely.

Atrazine residues (parent only) would also be found by the analytical methods used in the FDA Total Dietary Studies. No residues of atrazine have been found in any commodity in these studies at a limit of detection of 0.05 ppm.

In order to estimate likely average residue of atrazine plus its chlorometabolites in guava and pineapples, we have examined residue data for commodities in which all metabolites were measured, and have specifically examined commodities in which detectable residues of parent and at least one metabolite were found. Two trends were evident. First, the percentage of metabolites present relative to the total residue generally increased with increasing PHI. The rate of this percentage increase varied with commodity and with time of application. Secondly, a higher percentage of metabolites is found in samples with lower combined residues than with higher combined residues. This may be linked to the first conclusion since total residues decreased with time (although they did not appear to be linked in all cases). The percentage of metabolites ranged from 0 to >90%.

No PHI is stated on the atrazine label for guavas, and a 45-day PHI is required for applications to pineapples. Considering typical percentages of metabolites found in other commodities at 45-day PHI's and long (>60-day) PHI's, we have calculated likely average residues on guavas and pineapples assuming 70% and 40% respectively of the total residue consists of metabolites.

Detailed Considerations

Tolerances

The following tolerances are established for the combined residues of atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) and its metabolites 2-amino-4-chloro-6-ethylamino-s-triazine (G-28279), 2-amino-4-chloro-6-isopropyl-s-triazine (G-30033), and 2-chloro-4,6-diamino-s-triazine (G-28273)(40 CFR 180.220):

Commodity	Tolerance (ppm)
Grass, range	4
Orchardgrass (and hay)	15
Proso millet forage, fodder and straw	5
Proso millet, grain	0.25

(Tolerances continued on bottom of p. 5)

Table 1: Average Residues of Atrazine and Its Chlorometabolites In Agricultural and Processed Commodities

Commodity	Average Residues (ppm)	Percent Crop Treated
Corn, grain[2]	0.10	60-70
, forage	0.26	
, fodder	0.17	
, silage	0.14	
, processed frxns.[2]	0.10	
Sweet corn, fresh (K+CWHR)[2]	0.10	50-60
, forage	1.48	
, fodder	0.20	
, silage	0.24	
, cannery waste	0.10	
Guava	0.01	70-80[1]
Macadamia nuts	0.10	<50[1]
Pineapple, meat[2]	0.03	70-80[1]
, rind	0.03	
, forage	1.7	
, juice[2]	0.03	
, bran	0.03	
Sorghum, forage	2.02	60-70
, fodder	0.13	
, silage	0.47	
, grain[2]	0.13	
, feed stock	1.15	
, coarse grits	0.76	
, fine grits	0.82	
, flour	0.64	
, starch	0.21	
Sugarcane, whole cane	0.13	30-40
, forage	0.27	
, molasses	0.65	
, bagasse	0.95	
, refined sugar[2]	0.16	
Wheat, forage	0.43	<1
, straw	0.10	
, grain[2]	0.02	

(Continued next page)

Table 1: Average Residues of Atrazine and Its Chlorometabolites In Agricultural and Processed Commodities (Continued)

Commodity	Average Residues (ppm)	Percent Crop Treated
Wheat, grain	0.02	
, processed fxns.[2]	0.02	
Grass, range	0.90	<10[1]
Proso millet, forage	0.11	<1[1]
, fodder	3.37	
, grain[2]	0.68	
, bran	1.46	
, flour	0.35	
, hulls	0.68	
, meal	0.68	
Meat, fat and meat by-products (except liver) of cattle, goats, hogs, horses and sheep	0.01	NA
Liver of carttle, goats, hogs, horses and sheep	0.02	NA
Meat, fat and meat by-products of poultry	0	NA
Milk	0.004	NA
Eggs	0	NA

[1]Crude estimates (personal communication with Robert Torla, BUD, 8/22/88).
[2]These commodities are human food items whose average residue values should be used in the TAS analysis of dietary exposure/risk.

The following tolerances are established for residues of atrazine (parent only)(40 CFR 180.220):

Commodity	Tolerance (ppm)
Corn, forage and fodder	15
Corn, fresh (incl. K+CWHR)	0.25
Corn, grain	0.25
Guava	0.05
Macadamia nuts	0.25

(Table continued on next page)

Commodity	Tolerance (ppm)
Pineapples	0.25
Pineapple, forage and fodder	10
Rye grass, perennial	15
Sorghum, forage and fodder	15
Sorghum, grain	0.25
Sugarcane (incl. forage and fodder)	0.25
Wheat fodder and straw	5
Wheat, grain	0.25
Meat, fat and meat by-products of cattle, goats, hogs, horses, poultry and sheep	0.02
Eggs	0.02
Milk	0.02

Much of the residue data submitted includes data for the combined residues of atrazine and its chlorometabolites, and revised tolerances are proposed which include the proposed chlorometabolites in the tolerance expressions (for all commodities except guava and pineapples). Consequently, all of the estimates in Table 1 are for combined residues of atrazine and its chlorometabolites.

Product Chemistry

The process-related impurities formed in the manufacture of technical atrazine are listed in the Confidential Appendix. These data were submitted in response to deficiencies previously cited in the Registration Standard, and are assigned MRID No. 405665-01 (ref. 31). These data will not be formally reviewed here but will be reviewed as part of the Second Round Review of the Atrazine Registration Standard. As discussed in the Confidential Appendix, concerns regarding impurities in technical atrazine will not be addressed in this dietary exposure assessment.

Registered Uses

The three formulations of atrazine currently used on food crops are AAtrex^R 4L (EPA Reg. No. 100-497, 4 lbs.a.i./gallon emulsifiable concentrate), Aatrex^R 80W (EPA Reg No. 100-439, 80% a.i. wettable powder), and Aatrex^R Nine-0 (EPA Reg. No. 100-585, 90% a.i. dispersible granule formulation). The use directions for the three formulations are similar.

Corn

The herbicide is applied to corn at the following times and rates:

-Pre-plant surface applications as either a single or split application using a total of no more than 2 lbs.a.i./A.
-Pre-plant incorporated as a single application at a maximum rate of 3 lbs.a.i./A.
-Preemergence application made at or shortly after planting at a maximum rate of 3 lbs.a.i./A.
-Post-emergence before weeds are 1.5 inches tall and before corn is 20-30 inches tall at a maximum rate of 2 lbs.a.i./A.

Ground applications are made in a minimum of 10 gallons of spray mixture per acre including 1 qt./A oil concentrate or 1 gal/A petroleum-derived oil. Oils are added to post-emergent (weed) applications. Aerial applications are made in a minimum of approximately 2 gal water (or spray)/A including 1/2 - 1 qt/A oil concentrate or 2 qts./A petroleum-derived oil. For problem weeds, applications may be made as late as layby at rates as high as 4 lbs.a.i./A with oil. Recommended application rates vary with soil types. The following restriction is imposed:

-Do not graze or feed forage from treated areas for 21 days following application.

<u>Sorghum (and sorghum-sudan hybrids)</u>

Atrazine formulations may be applied to sorghum as follows:

-pre-plant surface applications as either a single or split application using 0.53-0.80 lbs.a.i./A total.
-pre-plant incorporated applications within two weeks prior to planting at 1.6-2.4 lbs.a.i./A.
-preemergence applications at or shortly after planting at 1.6-2.4 lbs.a.i./A.
-post-emergence applications before weeds reach 1.5 inches height and up to "close-in" at 2-3 lbs.a.i/A.
-post-emergence with oil applications can be made either prior to boot when sorghum is 6-10 inches tall or after the 3-leaf stage (depending on location) at 1.2 lbs.a.i./A. Ground applications would be made with 1 gallon emulsifiable oil/A, and aerial applications with 0.5 lbs. emulsifiable oil/A.

The following restriction is included on the Aatrex^R labels:

-Do not graze or feed forage from treated areas for 21 days following application.

The recommended application rate depends on soil type. The types of applications which can be used also depend on location.

Proso millet

A single application per year can be made to proso millet at rates of 0.5-2.0 lbs.a.i./A depending on soil type. Applications are made either pre-plant incorporated or preemergence.

Rangeland

Aerial or ground applications of atrazine to rangeland may be made at application rates ranging up to 2.0 lbs.a.i./A (max. 1.0 lb.a.i./A for Fall applications). Treated grass cannot be cut for hay. Treated fields cannot be grazed for either 3 or 7 months following Spring and Fall applications respectively.

Sugarcane

Pre- and Post-emergent applications may be made to sugarcane at rates up to 4.0 lbs.a.i./A. A maximum of 4 applications per crop may be made, with a maximum of 16 lbs.a.i./A/crop cycle applied. Applications may be made no later than "close-in".

Macadamia nuts

Preemergent (weed) ground applications may be made to Macadamia nuts at 2-4 lbs.a.i./A and repeated as necessary. Applications may not be made during the harvest period.

Pineapple

Applications to pineapple may be made at rates up to 6.4 lbs.a.i./A after planting or following harvest, and at 1.6 lbs.a.i./A at 1-2 month intervals as needed. A maximum of 30 lbs.a.i./A/crop cycle may be applied, and a 45-day PHI is imposed.

Guava

Atrazine may be applied to established plantings of guava which are at least 18 months old. Applications should be made by directed spray at 2-4 lbs.a.i./A avoiding contact with foliage or fruit. Do not apply more frequently than at 4-month intervals, and apply a maximum of 8 lbs.a.i./A/year.

Wheat

Atrazine may be applied to wheat fields during the fallow year at rates up to 1.0 lbs.a.i./A using either aerial or ground equipment. Wheat may not be planted within 12 months of treatment. Applications may also be made at rates up to 1.6 lbs.a.i./A with the restriction that wheat may not be planted for 2 years following application.

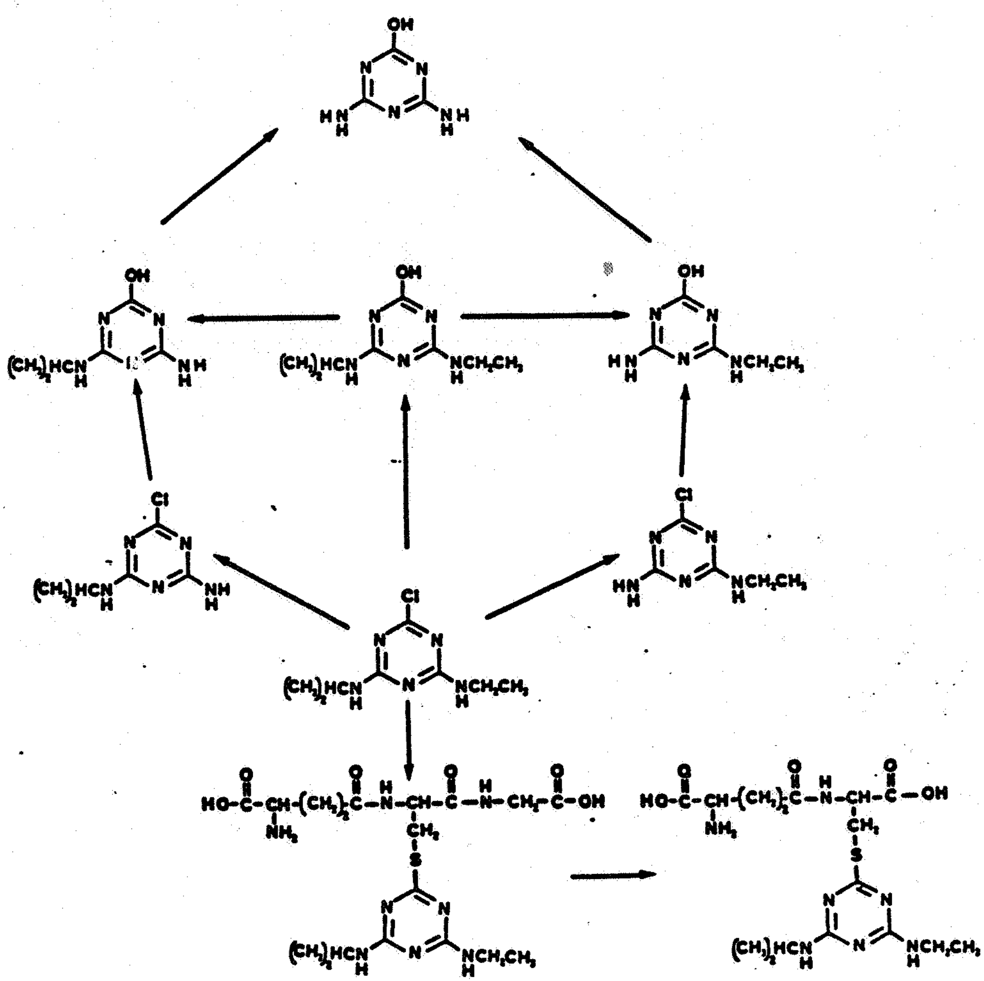
Metabolism

Plants

The metabolism of atrazine in plants was discussed in the Residue Chemistry Chapter of the Atrazine Registration Standard (7/11/83, pp. 2, 3) and in references 1-9. Atrazine is a systemic herbicide which is absorbed by roots (but not leaves), and translocated throughout the plant.

Metabolism occurs through primarily three mechanisms: N-dealkylation, 2-hydroxylation (i.e. hydrolysis of the C-Cl bond), and conjugation with glutathione or other endogenous plant components. This can then be followed by hydrolysis of the amino groups and/or breakdown of the glutathione (or other) side chain (see Table 2 for structures, chemical names, and code numbers for the metabolites). The predominant metabolic pathway is highly dependent on plant species. The major metabolic pathways for atrazine in plants are summarized in Figure 1.

Figure 1: Generalized Mechanism of Atrazine Metabolism in Plants



Metabolism in corn occurs primarily by hydroxylation and conjugation with glutathione with only a small amount of N-dealkylation; while metabolism in sorghum occurs primarily by glutathione conjugation and N-dealkylation with virtually no hydroxylation observed.

The available residue data for plants provide residues of only atrazine, per se, or combined residues of atrazine plus its chlorometabolites (G-28279, G-30033 and G-28273). In a recent discussion with TOX, it was concluded that the hydroxy metabolites of atrazine would be of concern if they were found to comprise a significant percentage of the total residue in plants (Atrazine Special Review Team meeting, 7/5/88).

Most of the available metabolism data are copies of studies taken from the literature and published prior to 1974. Adequate information is not available to quantify the relative levels of all of the various metabolites in plant species. However, the following summary table was submitted by the registrant as part of a metabolism review article (data for corn silage):

Residue Component	Percentage
Chlorotriazines	0
Hydroxyatrazine	29
De-ethyl hydroxyatrazine	12
De-isopropyl "	4
Soluble unknowns	27
Non-extractable	27
Total--->	99

Since hydroxyatrazine and other hydroxy metabolites were found to comprise a large portion of the total residue in at least one important commodity, and since TOX considers these metabolites to be of concern, DEB has requested that residue data for the hydroxy metabolites of atrazine be required in the Data Call-In (DCI) to be sent out as part of the Atrazine Special Review (M. Metzger, 7/12/88).

Formation of nitrosoatrazine in the presence of nitrite fertilizers in soils with low pH has been shown (Distribution, Movement, Persistence and Metabolism of N-Nitrosoatrazine in Soils and a Model Aquatic Ecosystem, J. Agric. Food Chem., Vol. 25, No. 5, 1977). However, at pH values greater than 4.5, little nitrosoatrazine is likely to be formed (<< 1%). Since commodities to which atrazine is applied are not tolerant to low soil pH's and are generally grown in soils with pH values greater than 5, it is unlikely that formation and uptake of nitrosoatrazine will occur to a measurable extent.

Ruminants

Numerous ruminant metabolism studies are available which reflect the dosing of cattle (refs. 11-13, 29), sheep (ref. 28) or goats (refs. 21-29) with either ^{14}C-atrazine, ^{14}C-G-28273, or ^{14}C-atrazine-treated commodities. These studies showed that most of the applied ^{14}C was excreted in the urine (ca. 50-60%) and feces (ca. 10-20%), with some transfer of residues to the tissues (liver>kidney>muscle>fat, ppm basis). A significant amount of residue was also transferred to milk.
In spite of the many studies performed, much of the ^{14}C in animal tissues remains uncharacterized. The following results were seen in most studies:

(1) The major component of the ^{14}C in milk is G-28273 (ca. 40-70%) with G-30033 and G-28279 (combined) contributing approximately 3-13%. Trace amounts of parent were found. The remaining activity in milk consisted of uncharacterized water-soluble metabolites and non-extractable components.

(2) Very little of the ^{14}C from animal tissues was characterized. In general, the organic tissue extracts contained only small percentages (<1/3) of the total activity indicating that atrazine and its less polar chlorometabolites may make up only a small portion of the total residue.

(3) Aqueous-extractable activity makes up a large portion of the total activity. However, most of the water soluble residue in tissues was not characterized.

(4) Following treatment of non-extractable residues with a protease, the percentage of non-extractable residues decreased and the percentage of aqueous soluble residues increased significantly. This indicates that a significant portion of the total tissue residue may be bound to peptides/proteins. Conjugation with lanthionine may be occurring, as well as conjugation with glutathione followed by degradation of the glutathione side chain.

These data indicate that the major metabolic degradation pathway for atrazine in ruminants is tissue-specific, and includes N-dealkylation and conjugation with endogenous tissue components. Formation of hydroxylated derivatives of atrazine was not seen in ruminant tissue. Numerous water-soluble components of the residue were seen on TLC plates but were not characterized. Generally, these were present at low levels. A summary of the metabolism of atrazine in animals is seen in Figure 2.

A study was submitted in which the atrazine metabolite ^{14}C-G-28273 was fed to goats (ref. 27). The resulting distribution of ^{14}C activity in tissues was similar to that seen in the ^{14}C-atrazine feeding studies. The major metabolite in milk was G-28273. Several aqueous-soluble TLC spots were observed but not characterized (small percentage of total residue). A large percentage of the total residue appeared to be bound to peptides/proteins.

The results of 2 additional studies were summarized (but the studies were not submitted) in which goats were fed either sorghum treated with ^{14}C-atrazine (aged residues) or corn ^{14}C-hydroxyatrazine biosynthesized metabolites. The registrant reports "little alteration of metabolites and low tissue deposition" in both cases.

Table 2: Chemical Names, Code Numbers and Structures of Atrazine and Its Metabolites

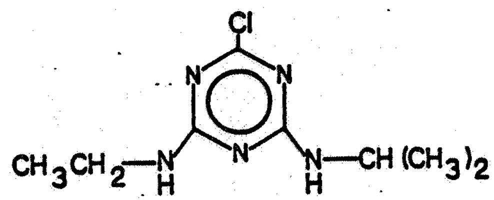
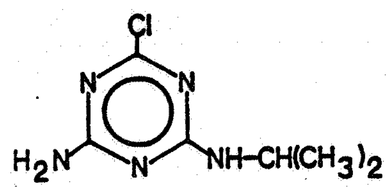
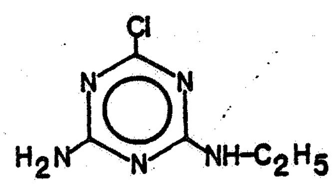
Chemical Name	Code No.	Structure
2-chloro-4-ethylamino-6-isopropylamino-s-triazine	Atrazine	
2-amino-4-chloro-6-isopropylamino-s-triazine	G-30033	
2-amino-4-chloro-6-ethylamino-s-triazine	G-28279	

Table 2: Chemical Names, Code Numbers and Structures of Atrazine and Its Metabolites (continued)

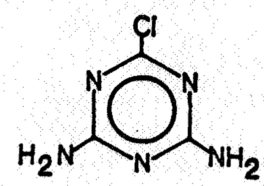
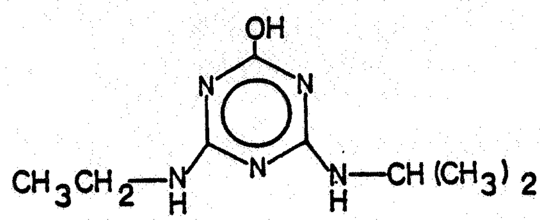
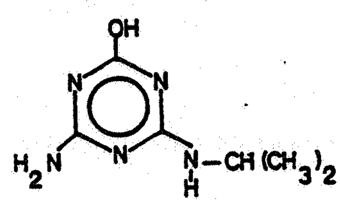
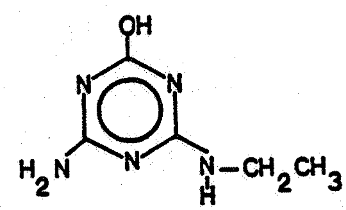
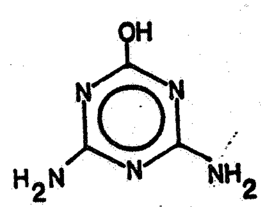
Chemical Name	Code No.	Structure
2,4-diamino-6-chloro-s-triazine	G-28273	
2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine (hydroxyatrazine)	G-34048	
2-amino-4-hydroxy-6-isopropylamino-s-triazine	GS-17794	
2-amino-4-hydroxy-6-ethylamino-s-triazine	GS-17792	
2,4-diamino-6-hydroxy-s-triazine (ammeline)	GS-17791	

Table 2: Chemical Names, Code Numbers and Structures of Atrazine and Its Metabolites (continued)

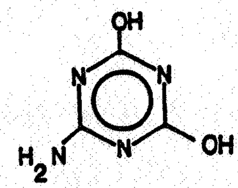
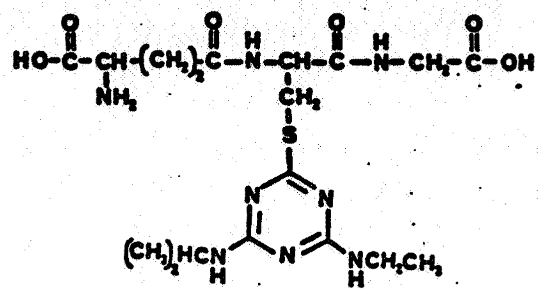
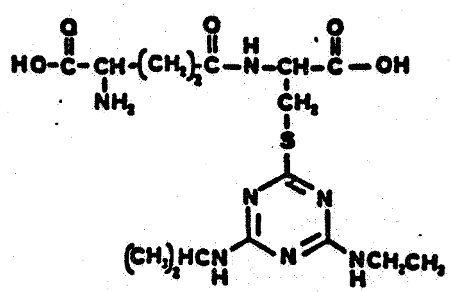
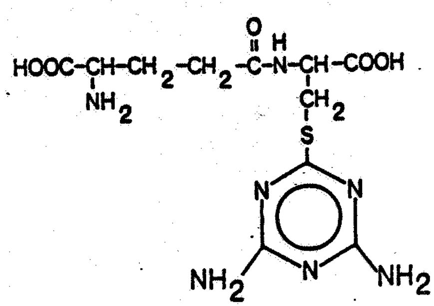
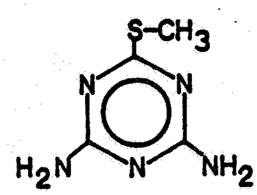
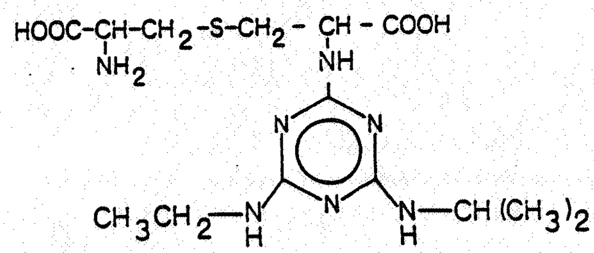
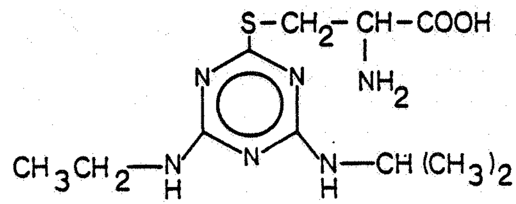
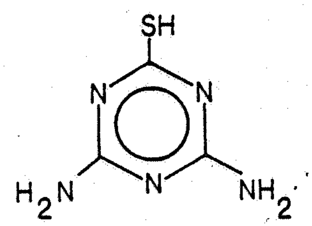
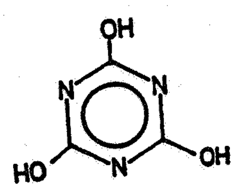
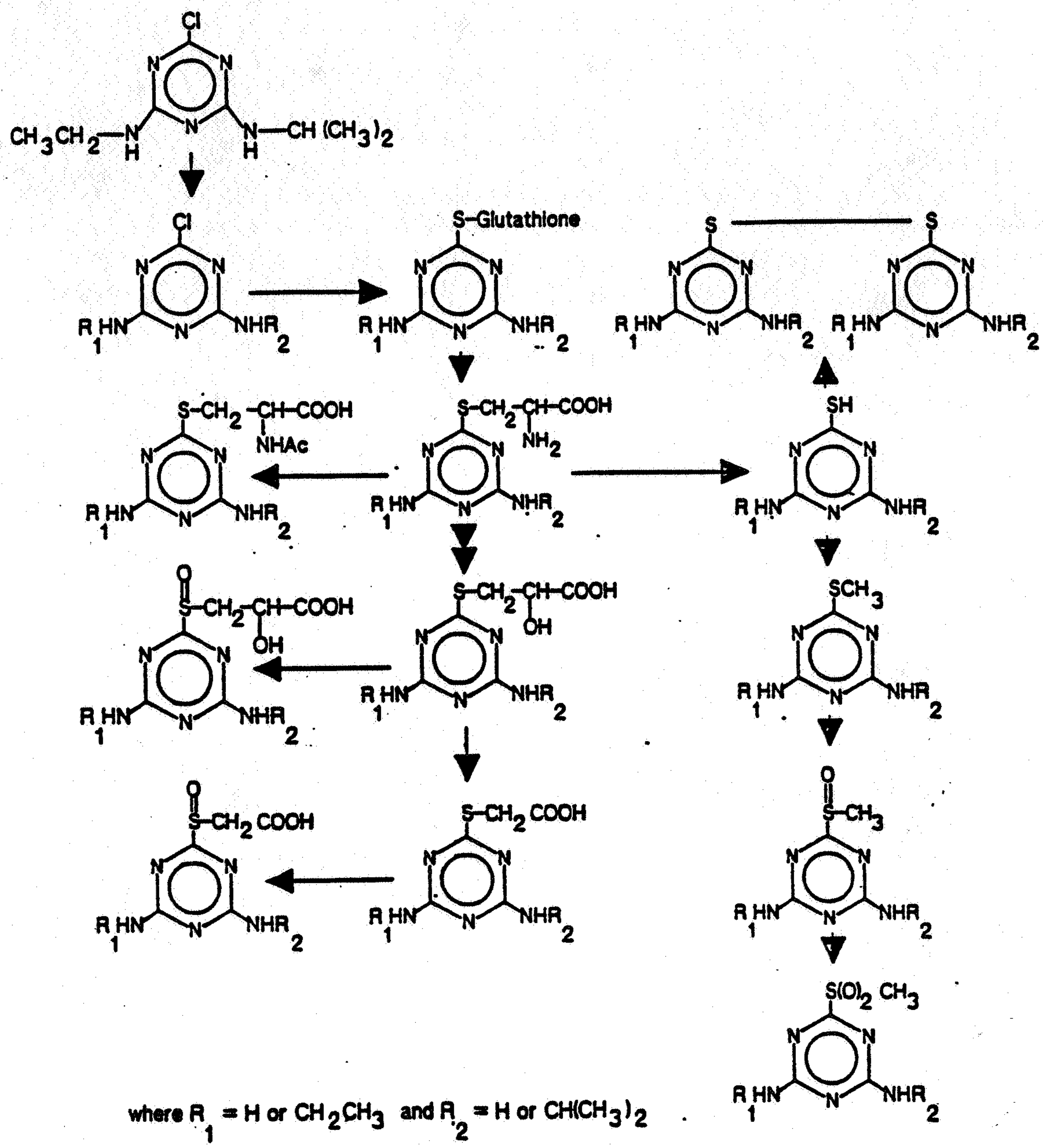
Chemical Name	Code No.	Structure
2-amino-4,6-dihydroxy-s-triazine		
Atrazine glutathione conjugate		
Atrazine glutamyl cysteinyl conjugate		
G-28273 glutamyl cysteinyl conjugate		
2,4-diamino-6-(methylthio)-s-triazine	GS-26831	

Table 2: Chemical Names, Code Numbers and Structures of Atrazine and Its Metabolites (continued)

Chemical Name	Code No.	Structure
Atrazine lanthionine conjugate		
Atrazine Cysteine conjugate		
G-28273 mercapto-derivative		
2,4,6-trihydroxy-s-triazine (cyanuric acid)	G-28521	

In summary, it appears that the major milk metabolite is G-28273 with lesser amounts of the mono-N-dealkylated metabolites and parent. Conjugation to peptides/proteins is also seen in milk. Few free metabolites are seen in tissue, these being water soluble and each comprising only a small percentage of the total residue. Numerous water-soluble metabolites are released after protease digestion indicating that conjugation with proteins/peptides is a major metabolic pathway in ruminant tissues.

Figure 2: Generalized Mechanism for Atrazine Metabolism in Animals



where R_1 = H or CH_2CH_3 and R_2 = H or $CH(CH_3)_2$

Poultry (Chicken)

Several poultry (chicken) metabolism studies were submitted (refs. 14-20, 29, 30). Most of the administered ^{14}C in these studies was eliminated in the excreta, although some was transferred to eggs and tissues (kidney>liver>egg>heart>meat>fat, ppm basis).

The following metabolites were found in various tissues: atrazine (parent), G-28273, G-28279, G-30033 and GS-26831. Parent was found only in egg yolks and excreta. G-28273 was the major metabolite found in most tissues (up to 65% of the total ^{14}C in egg yolk samples). Organic-solubles were low, and non-extractable residues accounted for a large percentage of the total residues in some tissues. Many aqueous-soluble components were not characterized.

The metabolism of atrazine in laying hens likely involves successive N-dealkylation to form G-28273, and glutathione conjugation to form S-peptide conjugates such as GS-26831 (S-methyl) and the Cysteine conjugate of atrazine (via conjugation with glutathione). A general depiction of the metabolism of atrazine in animals is shown in Figure 2 (taken from MRID No. 404313-45).

Analytical Methods

Ciba-Geigy Analytical Method No. AG-484 (ref. 34) was used in generating residue data for corn, proso millet and wheat commodities, as well as for Macadamia nuts. This method quantifies residues of parent, G-30033, G-28279 and G-28273 at detection limits of approximately 0.05 ppm for each metabolite in each matrix. Briefly, grain, forage and fodder samples are extracted with 20% water/80% methanol with reflux, and the extract is filtered and concentrated to the water layer. Oil samples are extracted with 20% water/80% acetonitrile, the extract is centrifuged discarding the oil, and the mixture is concentrated to the water layer. Soapstock samples are extracted with 25% hexane/75% ethyl acetate, the organic phase is removed and evaporated to dryness, the residue is dissolved in hexane and extracted into 20% water/80% acetonitrile, and the aqueous acetonitrile solution is concentrated to the water layer.

The water layer in each case is adsorbed onto an Extrelut column, and the column is eluted with 15% ethyl acetate/85% hexane isolating atrazine, G-30033 and G-28279 (fraction "A"), and with 50% ethyl acetate/50% hexane isolating G-28273 (fraction "B"). Fraction "A" is cleaned up on an Alumina B column, fraction "B" on a Sep-Pak column, and the eluates are reduced to dryness, the residue is dissolved in 95% ethyl acetate/5% methanol, and analysis is accomplished by capillary GC using a nitrogen-phosphorous detector.

Recovery data are shown in Table 3. Samples were fortified at levels of 0.05 to 0.5 ppm. Sufficient raw data/chromatograms were submitted to verify the 0.05 ppm limit of detection.

Table 3: Recoveries of Atrazine and Its Chlorometabolites from Proso Millet, Sorghum and Corn Commodities

Commodity	Average Recovery % / (Std. Deviation)			
	Atrazine	G-30033	G-28279	G-28273
Proso millet:				
grain	86.0 (9.6)	96.5 (6.6)	88.5 (2.6)	89.0 (22.6)
forage	107.7 (11.5)	103.3 (13.3)	97.7 (10.2)	90.7 (17.6)
fodder	102.7 (7.5)	107.7 (15.9)	98.7 (19.7)	103.0 (32.2)
Sorghum:				
grain	96.2 (9.9)	97.2 (5.3)	90.2 (10.1)	86.7 (19.5)
forage	107.0 (17.5)	101.0 (11.0)	95.3 (10.4)	99.8 (26.8)
coarse grits	132	127	132	96
fine grits	125	120	128	100
flour	95	124	117	89
feed	72	70	63	94
Corn:				
grain	93.6 (6.9)	95.1 (9.2)	91.3 (9.2)	70.3 (11.7)
forage	92.5 (8.3)	88.2 (7.1)	86.7 (9.2)	88.1 (11.8)
fodder	90.0 (10.9)	89.3 (10.0)	86.8 (9.2)	78.1 (20.6)
silage	98.7 (7.4)	95.5 (6.7)	88.6 (8.3)	87.3 (11.5)
ears, sweet	97.0 (4.6)	91.3 (6.1)	83.0 (1.0)	94.7 (31.5)
flour	100	73	101	92
germ	96	94	88	85
grits	97	94	85	83
meal	107	95	88	92
hulls	107	106	102	84
refined oil	82	90	81	87
crude oil	72, 77	78, 78	73, 81	83, 88
soapstock	72	97	96	56

Residue data for sugarcane and sugarcane commodities were generated using methods AG-295 (atrazine, G-30033 and G-28279) and AG-281 (G-28273). Method AG-295 involves extraction with either chloroform or 10% water/acetonitrile (reflux). If acetonitrile is used, an aliquot is diluted with water, and the residue is partitioned into dichloromethane. An aliquot of the chloroform or dichloromethane is cleaned-up on an alumina column, and the residue is analyzed by GLC using a Hall electrolytic conductivity detector. The reported limit of detection is 0.05 ppm. Recoveries at 0.05 ppm fortification ranged from 80-118% for atrazine, 91-126% for G-30033, and 80-126% for G-28279.

AG-281 involves extraction with methanol, partitioning against hexane, and evaporation to dryness followed by liquid-liquid partitioning and GLC analysis. The reported limit of detection is 0.10 ppm. Reported recoveries at 0.10 ppm fortification ranged from 80-113%.

The analytical method used to determine residues of atrazine (parent only) in pineapples was a spectrophotometric method submitted with PP#7F0620. The method used for determination of residues of atrazine (parent only) in guava was a GC method using an N-specific ECD (see PP#0E2398). Both of these methods were reviewed in the Atrazine Registration Standard (Residue Chemistry Chapter) and are considered adequate for data collection.

Residue data for range grass were generated using three analytical methods: AG-269, AG-232A and AG-396. These methods were reviewed with PP#3F2870 and are considered adequate for collection of residue data for atrazine and its chlorometabolites (see M. J. Bradley, 11/4/83).

The analytical methods used to determine residues of atrazine and its chlorometabolites in animal tissues, eggs and milk are analytical methods AG-463, AG-476 and AG-476 with modifications (ref. 36).

Method AG-463 determines residues of atrazine and its chlorometabolites in milk (ref. 35). Milk protein is precipitated from milk by the addition of acetone. The precipitate is removed, and the supernatant is cleaned-up on an Extrelut column. The eluate is reduced to dryness, redissolved in toluene, and analyzed by GC using a Nitrogen-phosphorous detector. The reported limits of detection are 0.01 ppm for each compound (combined = 0.04 ppm). Recoveries ranged from 80-131% at 0.01-0.10 ppm fortification levels.

Animal tissue and egg residues were determined using method AG-476 with or without modification (depending on tissue). Briefly, this method involves extraction with 50% acetone/water, followed by removal of the acetone from the supernatant at reduced pressure, and clean-up of the aqueous material on an Extrelut column. The eluate is concentrated to dryness and dissolved in toluene for capillary GC analysis using a nitrogen-phosphorous detector. The reported limits of detection are 0.01 ppm for each compound (combined = 0.04 ppm). Recoveries ranged from 59-124% at fortification levels of 0.01-5.0 ppm.

Storage Stability

Storage stability data are summarized in Table 4. Corn commodities fortified at 1.0 ppm, and meat, milk and eggs fortified at 0.25 ppm show no degradation of atrazine or its chlorometabolites at storage times of 186-215 days for most commodities (freezer temperatures not provided). Some degradation was seen for all metabolites, but particularly for G-28273, in beef liver and eggs (refs. 38, 39).

Table 4: Atrazine Storage Stability

Commodity	Storage Time (days)	% Recovery Atrazine	G-28279	G-30033	G-28273
Corn silage	0	99, 99	95, 98	94, 95	91, 89
	110	109,110	110,106	113,109	100, 85
	186	111, 92	107, 95	108,100	92, 99
Corn grain	0	98, 94	93, 88	94, 94	122,116
	110	103, 99	101,100	102,104	100,111
	186	106, 96	111,107	113,109	102, 93
Sweet corn ears	0	100, 96	97, 95	94,94	149, 108
	110	95, 94	102, 98	103,100	98, 94
	186	106,101	100, 96	104,100	94,113
Corn meal	0	94, 91	90, 88	96, 88	121,100
	121	112,111	107,109	103,108	96, 96
	187	98, 78	114,114	114,114	104,116
Corn flour	0	97, 92	95, 89	98, 92	109,107
	121	101,106	107,112	108,114	94,102
	187	102,102	102,103	107,102	92,104
Corn oil, crude	0	111,114	108,134	112,135	91, 91
	102	127,137	126,140	129,141	110, 96
	187	110,121	115,123	114,125	110, 96
Corn, soapstock	0	104,139	116,117	114,125	108, 83
	93	103, 87	109, 93	109, 90	77, 98
	208	108,112	107,113	114,116	96, 96
Beef tenderloin	0	104,104	104,104	104,104	104, 96
	137	112,104	104,100	104, 96	100, 96
	198	100, 92	96, 92	100, 92	84, 88
Beef liver	0	120,116	124,124	120,124	88,104
	125	96,104	88,100	76, 92	52, 52
	204	92, 84	88, 80	88, 80	44, 32
Beef fat	0	108,100	108,104	112,100	104, 96
	133	96, 96	100,100	100,100	100, 96
	199	96,108	104,104	104,112	104,104
Poultry lean meat	0	112, 92	108, 96	104, 92	116,124
	114	80, 80	80, 80	80, 80	92, 88
	201	100, 96	92, 92	92, 88	100, 92
Milk	0	112,108	112,112	112,112	104,104
	140	104,108	96,104	100,104	100,108
	215	96, 96	100, 96	104,104	100,100
Eggs	0	96, 96	100,100	96, 92	108,108
	118	76, 72	72, 66	64, 64	80, 76
	201	88, 92	84, 92	76, 84	64, 72

Additional data summarized in the Atrazine Registration Standard (Residue Chemistry Chapter, p. 11) indicate that residues of atrazine (parent only) and hydroxyatrazine are stable in sorghum samples (20 days, -15^{o}C) and milk samples (73 days, -10^{o}C) respectively.

Storage times for samples obtained in residue field trials ranged up to approximately 2 years for some commodities (corn, sorghum) and were not stated for others including pineapples. The available storage stability data reflect storage periods for at most 208 days (approx. 7 months). Since no degradation was seen at these storage times, for the purposes of this dietary exposure assessment only, we will assume no degradation of residues in stored plant samples. The additional storage stability data which the registrant states is currently being generated should be provided to DEB when completed. Additional storage stability data for plant commodities other than small grains (e.g. pineapples) should be provided so that residue degradation during storage in other types of crops can be determined.

Storage times for samples obtained in animal feeding studies ranged from approximately 3-5 months for milk to 12-20 months for animal tissues and eggs. This would not affect calculation of the average tissue residues in poultry and eggs since transfer of residues and dietary exposure is very low. However, this will affect calculations of average residues in cattle muscle and liver. Utilizing the available storage stability data and storage times for these commodities, we estimate that residues degraded during storage such that 25% and 80% of the original residue present in liver and meat respectively was present at the time of analysis. Average residues calculated for these commodities were corrected using these values.

Residue Data

Corn (Field and Sweet)

Residue data for field and sweet corn are summarized in Tables 5 and 6 (ref. 40). In calculating average residues likely to be found in corn commodities, the following PHI's will be assumed: 21 days for field and sweet corn forage since there is a 21-day grazing/feeding restriction included on the product labels; 100 days for field corn grain and fodder, and 60 days for sweet corn ears and fodder, both corresponding to the approximate times between "layby" (final allowed application), and harvest; 75 days for field corn silage corresponding to the time interval between "layby" and the time forage is customarily cut for silage; and 21 days for sweet corn silage corresponding to the 21-day grazing/feeding restriction on the product labels. Table 7 summarizes average values for those commodities and PHI's at maximum application rates.

In addition to the residue field trial data summarized in Tables 5 and 6, monitoring data for atrazine (parent only) are available from FDA as previously described.

Considering the available field trial data and FDA monitoring data, we consider the average combined residues included in Table

7 to be appropriate values for use in dietary exposure assessment for chronic toxicity at this time. We note, however, that it is likely that most of the atrazine residue in corn consists of the hydroxy metabolites, and no field trial data are available for these metabolites. RCB recently requested that a DCI be sent out asking that residue data for the hydroxy metabolites on various commodities be provided (M. Metzger, 7/6/88). Reevaluation of dietary exposure may be necessary when these data are received.

Corn Processed Fractions

Field corn was treated with Aatrex[R] 80W with oil at rates of 4.0 and 8.0 lbs.a.i./A with a PHI of 132 days. No detectable residues of atrazine or its chlorometabolites were found in grain or in any processed fraction including hulls, germ, grits, meal, flour,

Table 5: Residues of Atrazine and Its Chlorometabolites In Field Corn and Field Corn Commodities

Commodity	Appl. Rate lbs./A	PHI (days)	Residue Range (ppm) Atrazine	G-30033	G-28279	G-28273	Combined
Field corn, grain	1.6	133-204	<0.05-0.05	<0.05	<0.05	<0.10	<0.25,0.15
	2.0	96-179	<0.05	<0.05	<0.05	<0.10	<0.25
	2 + 2	97-140	<0.05	<0.05	<0.05	<0.10	<0.25
	4.0	97-170	<0.05	<0.05	<0.05	<0.05-<0.10	<0.25
	8.0	132	<0.05	<0.05	<0.05	<0.05	<0.20
, forage	1.6	64,66	<0.05	<0.05	<0.05	<0.10	<0.25
	2.0	48-109	<0.05	<0.05-0.06	<0.05	<0.10-0.22	<0.15-0.31
	2 + 2	10,11	<0.05-4.10	<0.05	<0.05	<0.10	<0.25-4.20
	3.0	0	106-354	-	-	-	106-354
		7	0.18-0.69	<0.05	<0.05	-	0.23-0.74
		14	0.05-0.44	<0.05	<0.05	-	0.10-0.49
		21	<0.05-0.47	<0.05	<0.05	<0.05-<0.20	<0.15-0.62
		28	<0.05-0.11	<0.05	<0.05	<0.05	<0.15-0.16

(Table continued next page)

Table 5: Residues of Atrazine and Its Chlorometabolites In Field Corn and Field Corn Commodities (continued)

Commodity	Appl. Rate lbs./A	PHI (days)	Residue Range (ppm) Atrazine	G-30033	G-28279	G-28273	Combined
	4.0	0	136-531	-	-	-	136-531
		7	0.32-7.40	<0.05	<0.05-0.19	-	0.37-7.62
		14	0.08-2.80	<0.05-0.05	<0.05-0.06	-	0.13-2.94
		19-22	<0.05-2.80	<0.05	<0.05-0.06	<0.05-0.07	<0.08-2.88
		28	<0.05-1.40	<0.05	<0.05	<0.05-0.23	<0.08-1.68
	8.0	21	<0.05	<0.05	<0.05	<0.05	<0.20
,fodder	1.5,1.6	133-204	<0.05	<0.05	<0.05	0.10-0.10	<0.15-0.18
	2.0	96-170	<0.05-0.19	<0.05	<0.05	<0.10-0.39	<0.15 0.46
	2 + 2	97-140	<0.05-0.46	<0.05	<0.05	<0.10	<0.25 0.56
	3.0	77-148	<0.05-0.07	<0.05	<0.05	<0.10-0.07	<0.25-0.19
Field corn, ,fodder	4.0	69-97	<0.05-1.80	<0.05-0.06	<0.05	<0.05-0.20	<0.05-1.88
		101-170	<0.01-1.30	<0.05	<0.05	<0.05-0.26	<0.20-1.30
	8.0	132	<0.05	<0.05	<0.05	<0.05	<0.20
,silage	1.5,1.6	89-105	<0.05	<0.05	<0.05	<0.10	<0.25
	2.0	67-124	<0.05	<0.05	<0.05	<0.10-0.20	<0.05-0.28
	2 + 2	32-94	<0.05-1.30	<0.05	<0.05	<0.10	<0.25-1.40
	3.0	58-96	<0.05-0.06	<0.05	<0.05	<0.10	<0.25-0.11
	4.0	48-71	<0.05-1.80	<0.05	<0.05	<0.10-0.44	<0.15-1.85
		85-127	<0.05	<0.05	<0.05	<0.10-0.08	<0.15-0.18
	8.0	71	<0.05	<0.05	<0.05	0.07	0.14

crude oil (solvent extracted), crude oil (expeller), refined oil, refined bleached oil, refined bleached deodorized oil and soapstock (limit of detection for combined residues 0.20 ppm). Select oil and grain samples were reanalyzed using an analytical method with a lower limit of detection (0.01 ppm). The only detectable residues found were in grain (G-28279, 0.02 ppm) and refined bleached deodorized oil (G-28279, 0.01 ppm) indicating that the concentration factor for G-28279 in refined bleached deodorized oil is 1/2X.

Insufficient information is available to determine concentration factors for each metabolite in each processed commodity since all but 2 of the residues determined were non-detectable. However, since no detectable residues were found in any processed commodity (except refined bleached deodorized oil at 0.01 ppm) at a more sensitive limit of detection than that used in the residue field trials (0.05 ppm or 0.20 ppm for combined residues), for the purposes of this dietary exposure assessment we will assume that residues do not concentrate in the processed corn fractions examined to a level greater than the average residue in grain. We, therefore, conclude that 0.10 ppm is a conservative estimate of the average residue likely to be found in processed corn fractions for use in chronic dietary exposure assessment.

Table 6: Residues of Atrazine and Its Chlorometabolites In Sweet Corn and Related Commodities

Commodity	Appl. Rate lbs./A	PHI (days)	Residue Range (ppm) Atrazine	G-30033	G-28279	G-28273	Combined
Sweet corn, ears ,forage	1.5-4.0	35-116	<0.05	<0.05	<0.05	<0.05, <0.10	<0.20, <0.25
	2.0	10	4.3-9.7	<0.05	<0.05	<0.10	4.4-9.8
		30	<0.05-0.12	<0.05	<0.05	<0.10	<0.25-0.22
		43-60	<0.05	<0.05	<0.05	<0.10	<0.25
	2 + 2	10	0.10-0.65	<0.05	<0.05	<0.10	<0.20-0.75
		37-52	<0.05	<0.05	<0.05	<0.10	<0.25
	3.0	0	113	<0.05	<0.05	<0.10	113.05
		7	8.4	<0.05	<0.05	<0.10	8.45
		14	0.70	<0.05	<0.05	<0.10	0.75
		21	0.23	<0.05	<0.05	<0.10	0.28
		28	0.11	<0.05	<0.05	<0.10	0.16

(Table continued next page)

Table 6: Residues of Atrazine and Its Chlorometabolites In Sweet Corn and Related Commodities (cont.)

Commodity	Appl. Rate lbs./A	PHI (days)	Residue Range (ppm) Atrazine	G-30033	G-28279	G-28273	Combined
, forage (cont.)	4.0	0	134-206	<0.05	<0.05	<0.10	134-206
		7	12.0-37.0	<0.05	<0.05	<0.10	12.1-37.0
		14	0.98-5.3	<0.05	<0.05	<0.10	1.08-5.40
		21	0.55-1.7	<0.05	<0.05	<0.10	0.65-1.80
		28	0.22-1.7	<0.05	<0.05	<0.10	0.32-1.80
, fodder	2.0	42-116	<0.05-0.06	<0.05	<0.05	<0.10-0.12	<0.25-0.23
	3.0	36	0.30	<0.05	<0.05	-	0.35
	4.0	36	0.08-1.50	<0.05	<0.05	<0.10	0.13-1.6
		75	<0.05	<0.05	<0.05	<0.10	<0.25
, silage	1.5,1.6	61,89	<0.05	<0.05	<0.05	<0.10	<0.25
	2 + 2	68	<0.05	<0.05	<0.05	<0.10	<0.25
	4.0	35-48	<0.05-0.60	<0.05	<0.05	<0.05	<0.20-0.68
		63-93	<0.05	<0.05	<0.05	<0.05-0.13	<0.20-0.20

Residue data for corn starch are not available (only a dry milling processing study has been submitted). Because some of the atrazine metabolites are water soluble (particularly G-28273), some residues could be removed in the wet milling process. In the absence of residue data, we will assume that most of the residue is removed in the milling process and does not concentrate in the starch. Therefore, for the purposes of this chronic dietary exposure assessment, we conclude that the combined average residue of atrazine and its chlorometabolites likely to be found in corn starch is 0.10 ppm.

Sweet corn cannery waste can be used as feed for cattle. In the absence of residue data for cannery waste, we will extrapolate from residue data for sweet corn ears. Since no detectable residues were found in sweet corn ears, we conclude that it is unlikely that detectable residues will be found in cannery waste. We, therefore, will estimate average residues in cannery waste to be 1/2 the analytical method limit of detection (1/2 LOD = 0.10 ppm) as with sweet corn ears.

Table 7: Average Residues of Atrazine and Its Chlorometabolites In Corn at Maximum Application Rates and Minimum PHI's

Commodity	PHI (days)	Avg. Combined Residue (ppm)
Field corn, grain	100	0.10[1]
, forage	21	0.26
, fodder	100	0.17
, silage	75	0.14
Sweet corn, ears	60	0.10[1]
, forage	21	1.48
, fodder	60	0.20
, silage	21	0.24
, cannery waste	-	0.10[2]

[1]Value represents 1/2 the combined limit of detection, no detectable residues found.
[2]Value represents 1/2 the combined limit of detection, average value estimated from residues found in sweet corn ears.

Guava

Residue data for guava were submitted with PP#0E2398 (Acc. No. 099550). Either 3 or 5 applications were made to guava trees at 2, 4 or 8 lbs.a.i./A/app. Residues (parent only) ranged from <0.002 to 0.011 ppm. Assigning non-detectable residues a value of 1/2 the limit of detection (1/2 LOD = 0.001 ppm), the average residues for 3 applications at 4.0 lbs.a.i./A (ca. 1.5X) was 0.003 ppm.

However, only residues of atrazine, pre se, were measured in this study. Based on our discussion in the Summary, the chlorometabolites of atrazine would account for approximately 70% of the residue. Therefore, we calculate an average combined residue of atrazine and its chlorometabolites in guava of 0.01 ppm.

Guava commodities are not major animal feed items. Therefore, secondary residues are not likely to result in animal tissues, milk or eggs as a result of the use of atrazine on guavas.

Macadamia Nuts

Either 3 or 4 applications of atrazine (80W or Nine-0 formulations) to Macadamia nut trees were made at the maximum application rate of 4.0 lbs.a.i./A (ref. 41). The intervals between applications were approximately 1 1/2 and 6 months for 3 applications, and 1 1/2, 1 1/2 and 4 1/2 months for 4 applications. Nuts were harvested 14 days after the final application. No detectable residues were found in the 9 nutmeat samples obtained at a combined limit of detection of 0.20 ppm (0.05 ppm for atrazine and each chlorometabolite). For the purposes of this dietary exposure assessment, we will assume an average residue in Macadamia nuts of 1/2 the combined limit of detection (1/2 combined LOD = 0.10 ppm).

Pineapples

Residue data for pineapples (parent only) are summarized in table 8 (from PP#7F0620). Although the raw agricultural commodity for pineapples is the whole fruit including meat and rind, for this dietary exposure assessment, we will estimate residues in meat and rind separately since only the meat is generally included in the human diet. Assuming application at the maximum rate, a 45-day PHI, and 40% additional residues to account for the chlorometabolites which were not analyzed for (see Summary), we estimate that the following values represent average residues likely to be found in pineapple commodities:

Pineapple meat..............0.03 ppm
" rind..............0.03 ppm
" forage............1.7 ppm

Table 8: Residues of Atrazine (Parent Only) in Pineapple Fruit and Forage

Commodity	App. Rate (lbs.a.i./A)	PHI (Days)	Atrazine Residues (ppm)
Pineapple meat	4.0, 9*4.0, 10*4.0, 8.0, 50.0	11-474	<0.04
	16.0	11	<0.04, 0.14
	32.0	11	<0.04, 0.13
Pineapple rind	4.0	11	<0.04, 1.08
		474	<0.04
	8.0	11	0.95, 1.12
		474	<0.04
	16.0	11	1.06, 4.70
		474	<0.04
	32.0	11	1.89, 2.40
		21	<0.04
		56	<0.04
	(8, 9 or 10) * 4.0	152-336	<0.04

(Table continued next page)

Table 8: Residues of Atrazine (Parent Only) in Pineapple Fruit and Forage (cont.)

Commodity	App. Rate (lbs.a.i./A)	PHI (Days)	Atrazine Residues (ppm)
Pineapple foliage	8.0	47	0.3 - 3.5
		91	0.2 - 1.2
		126	0.1 - 0.4
		294-482	<0.04
	16.0	47	1.8 -19.0
		91	1.0 - 1.6
		126	1.5 -35.0
		294-482	<0.04
	32.0	47	1.7 - 4.9
		91	0.6 - 1.2
		126	1.5 -35.0
		294	<0.04
	8 * 4.0	299	<0.04

Pineapple Processed Fractions

No residue data are available for the pineapple processed fractions, bran and juice. However, since no detectable residues would be expected in pineapple meat at a 45-day PHI, it is unlikely that detectable residues would be found in juice. Therefore, we estimate average residues in pineapple juice of 0.03 ppm (1/2 the limit of detection + 40% additional residues to correct for atrazine metabolites which were not measured in these studies).

Pineapple bran is composed primarily of the outer shell and sometimes also the core of the fruit. Therefore, based on the residue data for pineapple rind and meat shown in Table 8, we estimate average residues in pineapple bran of 0.03 ppm.

Sorghum

Residue data for sorghum are summarized in Table 9. In calculating the average residues likely to be found in sorghum commodities, the following minimum PHI's will be assumed: 21 days for forage, 65 days for grain and fodder, and 50 days for silage. The 21-day PHI for forage reflects the 21-day grazing/feeding restriction on the product labels. The 65-day PHI for grain and fodder correspond to the approximate time between "close-in" and harvest. The 50-day PHI for silage corresponds roughly to earliest time sorghum is customarily cut for silage. Table 10 summarizes the average residues for these commodities and PHI's at the maximum applications rate. These averages were calculated assigning samples with non-detectable residues values at 1/2 the analytical method limit of detection.

As discussed previously, less than 10 detectable residues of atrazine have been reported in FDA surveillance data since 1978 (<0.05% of the samples analyzed).

Based on the field trial data as well as the FDA surveillance data, we conclude that the average combined residues shown in Table 10 are appropriate to use in dietary exposure assessment for chronic toxicity.

Sorghum Processed Fractions

Sorghum was treated at application rates of 3.0 and 6.0 lbs.a.i./A (1X and 2X rates) utilizing a 113-day PHI (minimum PHI = approximately 65 days). No detectable residues were found of parent or any metabolite at the 0.05 ppm limit of detection. The chromatograms were, therefore, reexamined at a "non-validated limit of detection" of 0.02 ppm. Detectable residues of G-28273 only were found. These data are summarized in Table 11. Since detectable residues were found for only one metabolite, concentration factors cannot be determined for other components of the residue in these matrices (a processing study in which atrazine is applied at exaggerated rates and utilizing the minimum PHI may be required to show detectable residues and residue concentration of all metabolites).

Based on these limited data, and for the purposes of this chronic dietary exposure assessment only, we will assume that the combined residues will concentrate in processed commodities similar to the concentration of G-28273. Therefore, we conclude that the residue values shown in Table 11 which assume

Table 9: Residues of Atrazine and Its Chlorometabolites In Sorghum Commodities

Commodity	Appl. Rate lbs./A	PHI (days)	Residue Range (ppm) Atrazine	G-30033	G-28279	G-28273	Combined
Sorghum, forage	3.0	0	68.0-238	-	-	-	68.0-238
		7	0.20-9.0	<0.05-0.22	<0.05-0.05	<0.10-<0.20	0.57-9.1
		14	0.20-0.90	0.07-0.23	<0.05-0.11	<0.10-0.14	0.60-1.10
		21-22	<0.05-17.0	<0.05-0.25	<0.05-0.11	<0.05-0.47	<0.20-17.0
		28	0.09-0.18	0.05-0.24	<0.05	<0.10-0.17	0.19-0.50
		69	<0.05	<0.05	<0.05	<0.10	<0.25
	6.0	22	1.10	0.13	<0.05	<0.05	1.28

(Continued next page)

Commodity	Appl. Rate lbs./A	PHI (days)	Residue Range (ppm) Atrazine	G-30033	G-28279	G-28273	Combined
Sorghum, forage (cont.)	2.0	0	43-172	-	-	-	43-172
		7	0.82-9.4	<0.05-0.15	<0.05-0.09	<0.05-<0.10	1.11-9.48
		14	0.26-1.8	<0.05-0.17	<0.05-0.06	<0.05-<0.10	0.53-1.88
		21	0.21-0.40	<0.05-0.16	<0.05-0.06	<0.05-0.10	0.28-0.61
		28	0.14-0.23	<0.05-0.22	<0.05	<0.05-0.10	0.22-0.58
		46-80	<0.05	<0.05	<0.05	<0.05-<0.10	<0.20-<0.25
	4.0	0	4.1, 4.2	-	-	-	4.1, 4.2
		7	92.0	-	-	-	92.0
		14	0.10	-	-	-	0.10
		28	0.06, 0.09	-	-	-	0.06, 0.09
	1.6	28-36	<0.05-1.1	<0.05	<0.05	<0.05-0.08	<0.20-1.2
		76-92	<0.05	<0.05	<0.05	<0.05-<0.10	<0.20-<0.25
	3.2	28-36	<0.05-1.1	<0.05-0.05	<0.05	<0.05-0.07	<0.20-4.18
,fodder	3.0	70-113	<0.05-1.20	<0.05-0.09	<0.05	<0.05-0.42	<0.20-1.30
	2.0	87-128	<0.05	<0.05-0.05	<0.05	<0.10	<0.15-0.15
	6.0	113	<0.05	<0.05	<0.05	<0.05	<0.20
	1.6	55-141	<0.05-0.07	<0.05-0.05	<0.05	<0.05-0.09	<0.20-0.19
	3.2	97-122	<0.05	<0.05	<0.05	<0.05-0.06	<0.20-0.14
,silage	3.0	52,60	<0.05	<0.05-0.17	<0.05	<0.10-0.17	<0.15-0.39
	2.0	52,60	<0.05-0.14	<0.05	<0.05-0.07	<0.10	<0.15-0.20
	1.6	62-104	<0.05	<0.05	<0.05	<0.10	<0.25
,grain	3.0	69-113	<0.05	<0.05	<0.05	<0.05-0.14	<0.20-0.22
	2.0	69-132	<0.05	<0.05	<0.05-0.06	<0.10-<0.20	<0.15-0.16
	1.6	75-144	<0.05-0.07	<0.05	<0.05	<0.05-<0.10	<0.20-0.17
	3.2	97-122	<0.05	<0.05	<0.05	<0.05	<0.20

Table 10: Average Residues of Atrazine and Its Chlorometabolites in Sorghum at Maximum Application Rates and Minimum PHI's.

Commodity	PHI (days)	Avg. Combined Residues (ppm)
Sorghum:		
Forage	21	2.02
Fodder	65	0.13
Silage	50	0.47
Grain	65	0.13

concentration (or dilution) from an average residue of 0.13 ppm in sorghum grain, to be appropriate for use in chronic dietary exposure assessment.

Residue data for sorghum starch are not available (a wet milling processing study has not been submitted). In the absence of residue data for sorghum starch, we will assume that the wet milling process removes much of the residue of atrazine and its chlorometabolites since the metabolites, particularly G-28273, have significant water solubility. Therefore, we conclude that the average combined residue of atrazine and its chlorometabolites in sorghum starch is 0.13 ppm.

Table 11; Residues of Atrazine and Its Chlorometabolites in Sorghum Processed Commodities

Commodity	App. Rate (lbs.a.i./A)	Residues G-28273 (ppm)	Concen. Factor (CF)	Avg. CF	Likely Avg. Residue (ppm)
Grain	3.0	0.018	-	-	-
	6.0	0.030	-	-	-
Feed stock	3.0	0.021	1.17	-	
	6.0	0.034	1.13	1.15	0.15
Coarse grits	3.0	0.013	0.72	-	-
	6.0	0.024	0.80	0.76	0.10
Fine grits	3.0	0.015	0.83	-	-
	6.0	0.024	0.80	0.82	0.11
Flour	3.0	0.013	0.72	-	-
	6.0	0.017	0.57	0.64	0.08

Sugarcane

Residue data for sugarcane are summarized in Table 12 (from PP#3F2772/3H5371). Statistical analysis of these data predict half-lives in sugarcane for atrazine (parent only) ranging from approximately 6-27 days depending on application rate. Four samples had detectable residues of metabolites at PHI's consistent with this use. The maximum value found was 0.09 ppm for G-30033 at a PHI of 140 days. Assuming 1/2 the limit of detection for samples containing no detectable residues, average residues at PHI's of 90 days or greater ranged from 0.01-0.13 ppm (all application rates 1X or less). Based on this information, we estimate that the average residue likely to be found on sugarcane as a result of atrazine applications at registered rates is 0.13 ppm.

The average residue on sugarcane leaves for samples in which atrazine and its chlorometabolites were measures is 0.27 ppm. No residue data are available for forage, per se. However, since the leaves make up a large part of the sugarcane forage and contain higher residues than the cane, we will translate from leaves to forage and conclude that the average residue likely to be found in sugarcane forage is 0.27 ppm.

Sugarcane Processed Fractions

Residue data for sugarcane processed fractions are summarized in Tables 13 and 14. Residue data in table 13 reflect 3 applications of atrazine to sugarcane at 4 lbs.a.i./A/app. and an 87-day PHI. Data in Table 14 reflect concentration of residues in processed fractions when either cane or juice were fortified with atrazine or one of its chlorometabolites. Data in table 14 were used only to support data in Table 13 since determination of residue concentration using spiked commodities is not acceptable for systemic pesticides. Assuming 0.13 ppm combined residues of atrazine and its chlorometabolites in whole cane, we estimate the following average residues in sugarcane and its processed commodities:

Commodity	Combined Average Residue (ppm)
Sugarcane, whole cane	0.13 ppm
" molasses	0.65 ppm
" bagasse	0.95 ppm
" refined sugar	0.16 ppm

Table 12: Residues of Atrazine and Its Chlorometabolites In Sugarcane Commodities

Commodity	Appl. Rate lbs./A	PHI (days)	Residue Range (ppm) Atrazine	G-30033	G-28279	G-28273	Combined
Sugarcane	4+4+4/ 4+4+2.4	87-312	<0.04-0.05	<0.05-0.09	<0.05	<0.10	<0.25-0.16
	4+4+4 or 8+4	0,1	1.8-430	0.18	-	-	1.8-430
		7	0.50-157	0.21	-	-	0.50-157
		14	0.35-118	0.26	-	-	0.61-118
		29,30	<0.04-52.0	0.14	-	-	<0.04-52.0
		87	<0.04-0.05	0.05	-	-	<0.04-0.10
	8+4+4 or 8+8	1	282-1900	-	-	-	282-1900
		7	42.0-387	-	-	-	42.0-387
		14	26.0-263	-	-	-	26.0-263
		29	4.0-114	-	-	-	4.0-114
	8+8+8	1	818, 863	-	-	-	818, 863
		7	52.0, 191	-	-	-	52.0, 191
		14	46.0, 73.0	-	-	-	46.0, 73.0
		29	19.0, 28.0	-	-	-	19.0, 28.0
Sugarcane leaves	2+2+2 to 8+8+8	102-249	<0.04-0.08	<0.05-0.15	<0.05	<0.10-0.71	<0.25-0.89

Table 13: Residues of Atrazine and Its Chlorometabolites in Processed Sugarcane Fractions

Commodity	Atrazine Residues (ppm)	Concentration Factor	Average Concentration Factor
Whole cane	0.05, <0.04*	-	-
Bagasse	0.44, 0.23	8.8X, 5.8X	7.3X

(Continued next page)

(cont.) Commodity	Atrazine Residues (ppm)	Concentration Factor	Average Concentration Factor
Mud	0.06, 0.10	1.2X, 2.5X	1.8X
Mixed juices	0.08, 0.04	1.6X, 1.0X	1.3X
Clarified juices	0.11, 0.18	2.2X, 4.5X	3.4X
Syrup	0.27, 0.27	5.4X, 6.8X	5.9X
Molasses	0.28, 0.18	5.6X, 4.5X	5.0X
Sugar	0.04, 0.06	0.8X, 1.5X	1.2X

*Concentration factors assume 0.04 ppm in whole cane.

Table 14: Concentration Factors for Sugarcane Processed Fractions from Chopped Cane or Juice Spiked with Atrazine and Its Chlorometabolites at 0.1 or 0.2 ppm

Commodity	Average Concentration Factor				
	Atrazine	G-30033	G-28279	G-28273	Combined
Fortified cane:					
Bagasse	2.4	1.5	1.0	0.8	1.4
Settlings	0.4	0.6	0.6	0.7	0.6
Molasses	2.6	6.2	4.6	8.3	5.4
Raw sugar	0.2	0.6	0.2	0.2	0.3
Recryst. sugar	<0.2	<0.2	<0.2	<0.1	<0.2
Fortified juice:					
Settlings	1.0	1.1	1.1	1.0	1.0
Molasses	6.3	8.9	6.9	12.5	8.6
Raw sugar	0.4	0.3	0.3	0.2	0.3
Recryst. sugar	<0.3	<0.3	<0.3	<0.2	<0.3

Wheat

Residue data for wheat are summarized in Table 15 (ref. 34). Atrazine is registered for application to wheat fields during fallow years. Although no PHI is stated on the label, the registrant indicated that a minimum 12-month PHI is implied for forage, and a 650-700 day PHI for grain and straw. Table 16 summarizes the average residues for wheat commodities at these PHI's and the maximum application rate (1.0 lbs.a.i./A). These values were calculated assigning non-detectable residues a value of 1/2 the limit of detection.

Based on these data and on the FDA Surveillance Monitoring data, we conclude that the average combined residues for wheat commodities shown in Table 16 represent typical residues likely

Table 15: Residues of Atrazine and Its Chlorometabolites In Wheat Commodities

Commodity	Appl. Rate lbs./A	PHI (days)	Residue Range (ppm) Atrazine	G-30033	G-28279	G-28273	Combined
Forage	1.0	389-681	<0.05-0.29	<0.05-0.45	<0.05-0.07	<0.05-0.10	<0.20-0.86
Straw	1.0	658-731	<0.05	0.05-0.05	<0.05	<0.05-0.11	<0.20-0.21
Grain	1.0	658 731	<0.01	<0.01-0.01	<0.01	<0.01-0.10	<0.04-0.12

Table 16: Average Residues of Atrazine and Its Chlorometabolites in Wheat at Maximum Applications Rates and Minimum PHI's.

Commodity	PHI (days)	Avg. Combined Residues (ppm)
Forage	365	0.43
Straw	650	0.10
Grain	650	0.02

to be found in these commodities, and represent an estimate of the typical residues to which man and animals are likely to be chronically exposed.

Wheat Processed Fractions

Wheat grain samples with no detectable residues (<0.04 ppm) were processed into "rough", bran, shorts and germ, red dog, low grade flour, and patent flour. Since no detectable residues were found in any processed fraction or in grain, we cannot estimate residue concentration based on these data. However, for the purposes of this dietary exposure assessment only, we conclude that average residues in the processed fractions of wheat will be approximately the same as the average residues in wheat grain (0.02 ppm).

Range Grass

Tolerances are established for various grasses including perennial rye grass (15 ppm), range grass (4 ppm), orchardgrass (15 ppm) and orchardgrass hay (15 ppm). However, the registrations for use on rye grass and on orchardgrass have been cancelled because the registrant chose not to submit additional data required by the Atrazine Registration Standard (personal communication with Robert Taylor, PM-25, RD, 8/18/88).

Residue data for range grass are summarized in Table 17 (from PP#3F2870). Based on these data, and assuming applications at the maximum application rate and minimum PHI, we conclude that average combined residues of atrazine and its chlorometabolites on range grass resulting from registered uses would be 0.9 ppm.

Table 15: Residues of Atrazine and Its Chlorometabolites In Range Grass

Commodity	Appl. Rate lbs./A	PHI (days)	Residue Range (ppm) Atrazine	G-30033	G-28279	G-28273	Combined
Range grass, (Spring treatment)	1.0	0	63.0-390	-	-	-	63.0-390
		43	0.29, 0.34	0.24, 0.18	<0.05	<0.10	0.66, 0.54
		60-62	0.15, 3.5	<0.05-0.60	<0.05-0.31	<0.10-0.37	0.25-4.12
		91-93	<0.05-0.37	<0.05-1.1	<0.05-0.23	<0.10-1.3	<0.25-3.00
	2.0	0	64.0-315	-	-	-	64.0-315
		30-32	0.44-25.0	0.09-4.0	<0.05-0.82	<0.10-1.0	0.60-30.1
		60-63	<0.05-6.7	<0.05-1.3	<0.05-0.30	<0.10-2.0	<0.25-8.52
		90-99	<0.05-0.48	<0.05-1.1	<0.05-0.22	<0.10-1.2	<0.25-2.78
Range grass, (Fall treatment)	1.0	166-270	<0.05-2.3	<0.05-1.4	<0.05-0.48	<0.10-1.3	<0.25-5.00
	1.2	152-315	<0.05-10.0	<0.05-1.1	<0.05-0.18	<0.10-0.61	<0.25-11.3
	1.6	197-315	0.05-0.69	0.10-1.1	<0.05-0.32	<0.10-0.10	0.24-2.75
	2.0	152, 182	0.24, 0.11	0.25, 0.21	<0.05-0.05	0.16, 0.44	0.68, 0.82

Proso Millet

Residue data for proso millet are summarized in table 18 (ref. 44). Atrazine may be applied to proso millet only at or near planting (preemergent). Since the crop matures in 60-75 days, we will assume a 60-day PHI in calculating likely average residues in proso millet commodities. Table 19 summarizes the average residues at the maximum application rate and a 60-day PHI. These values were calculated assigning samples with non-detectable residues values of 1/2 the limit of detection.

Table 18: Residues of Atrazine and Its Chlorometabolites In Proso Millet Grass

Commodity	Appl. Rate lbs./A	PHI (days)	Residue Range (ppm) Atrazine	G-30033	G-28279	G-28273	Combined
Forage	2.0	32	0.05, 0.10	0.06, 0.14	0.10, 0.05	0.09, <0.05	0.43, 0.18
		51,71	<0.05	<0.05	<0.05	<0.05	<0.20
	4.0	32	0.05	0.06	0.05	<0.05	0.18
Fodder	2.0	87-109	<0.05-0.09	<0.05-0.17	<0.05-0.24	<0.05-0.35	<0.20-0.85
	4.0	87	0.08, 0.06	0.15, 0.11	0.17, 0.14	0.43, 0.29	0.83, 0.60
Grain	2.0	87-109	<0.05	<0.05-0.05	<0.05-0.10	<0.05-0.14	<0.20-0.32
	4.0	87	<0.05	<0.05	0.08	0.13	0.26

Table 19: Averages Residues of Atrazine and Its Chloro-Metabolites In Proso Millet at Maximum Application Rates and Minimum PHI's

Commodity	PHI (days)	Avg. Combined Residues (ppm)
Forage	60	0.11
Fodder	60	3.37
Grain	60	0.68

Based on these data and on FDA Surveillance Monitoring data, we conclude that the average combined residues shown in Table 19 represent average residues likely to be found in proso millet commodities resulting from registered uses of atrazine.

Proso Millet Processed Fractions

Residue data for proso millet processed fractions are summarized in Table 20. Based on the calculated concentration factors, and assuming average residues in grain of 0.68 ppm, we conclude that the average residues in proso millet processed fractions are those shown in Table 20.

No data are available for proso millet hulls or meal. Since the available data show residue concentration in bran (seed coat) and residue dilution in flour (produced from seed), we will assume

Table 20: Residues of Atrazine and Its Chlorometabolites in Proso Millet Processed Commodities

Commodity	App. Rate (lbs.a.i./A)	Combined Residues (ppm)	Concen. Factor (CF)	Avg. CF	Likely Avg. Residue (ppm)
Grain	2.0	0.165	-	-	-
		0.20	-	-	-
	4.0	0.26	-	-	-
		0.26	-	-	-
Bran	2.0	0.27	1.64		
		0.33	1.65		
	4.0	0.74	2.85		
		0.64	2.46	2.15	1.46
Flour (high ash)	2.0	<0.20	-	-	-
	4.0	0.133	0.52	0.52	0.35
Flour low ash)	2.0	<0.20	-	-	-
	4.0	0.135	0.52	0.52	0.35

for the purposes of this dietary exposure assessment that average residues likely to be found in hulls are the same as those likely to be found in whole grain. Additionally, we will assume that residues likely to be found in proso millet meal will be the same as those found in whole grain since the meal is composed primarily of grain.

Meat, Milk, Poultry and Eggs

Animal feeds which may contain residues of atrazine and its metabolites are summarized in Table 21. Proso millet commodities are excluded from this Table because only a small portion of the millet crop is likely to be treated with atrazine. Provided in the Table are both the average residues and the average residues corrected for percent crop treated. Starred (*) commodities in each column indicate those animal feeds which were used in determining the potential average dietary residues of atrazine for each animal.

A cattle feeding study was submitted in response to the Atrazine Registration Standard (refs. 45, 46). Eleven dairy cows were split into 4 groups with 2 control cows, 3 receiving 3.75 ppm atrazine in their diets, 3 receiving 11.25 ppm, and 3 receiving 37.5 ppm. One cow from each treatment group was sacrificed at days 14, 21 and 28. Milk was collected from each treatment group on days 1, 4, 7, 12, 19 and 26 after initiation of atrazine dosing.

Table 21: Residues of Atrazine and Its Chlorometabolites in the Diets of Cattle and Poultry

Feed	Average Residues (ppm)	Corrected[3,4] Average Residues (ppm)	(% in Diet), Residues in Diet: Cattle: Beef	Cattle: Dairy	Poultry: T/B[1]	Poultry: L/H[2]
Corn, grain	0.10	0.070	0.056 (80)	0.035 (50)	0.026* (37)	0.025* (36)
, forage	0.26	0.182	0.046 (25)	0.018 (10)	0	0
, silage	0.14	0.098	0.025 (25)	0.010 (10)	0	0
, fodder	0.17	0.119	0.030 (25)	0.012 (10)	0	0
Sweet corn, forage	1.48	0.888	0.222 (25)	0.089 (10)	0	0
,cannery waste	0.10	0.070	0.021 (30)	0.035 (50)	0	0
Pineapple, bran	0.02	0.016	0.006 (40)	0.006 (40)	0	0.009 (5)
, forage	1.0	0.80	0.160 (20)	0.320 (40)	0	0
Sugarcane, molasses	0.65	0.260	0.052* (20)	0.026* (10)	0.001* (3)	0.001* (4)
, bagasse	0.95	0.380	0.019* (5)	0.019* (5)	0	0
, forage	0.27	0.108	0.022 (20)	0.043 (40)	0	0
Wheat, grain	0.020	0.000	0	0	0	0
, forage	0.43	0.004	0.001 (25)	0.003 (70)	0	0
, hay	0.10	0.001	0	0.001 (60)	0	0
, straw	0.10	0.001	0	0	0	0
, processed fxns	0.02	0.000	0	0	0	0
Grass, range	0.90	0.090	0.068 (75)	0.063 (70)	0	0
Sorghum, grain	0.13	0.091	0.046* (50)	0.032* (35)	0.055* (60)	0.055* (60)
,fodder	0.13	0.091	0.023 (25)	0.046 (50)	0	0
, silage	0.47	0.329	0.082 (25)	0.165 (50)	0	0
, forage	2.02	1.414	0.354 (25)	0.707 (50)	0	0
Total dietary residues------->			0.471	0.784	0.082	0.081

(footnotes on next page)

[1]T/B = Turkeys/Broilers
[2]L/H = Laying hens
[3]Corrected for percent crop treated.
[4]See Table 1 for percent crop treated for each commodity.

No residues of atrazine , G-30033 or G-28279 were detected in any sample at any feeding level. Residues of G-28273 in cattle tissues and milk are summarized in Tables 22 and 23. Assuming that dietary residues of atrazine and its metabolites for beef and dairy cattle are 0.471 ppm and 0.784 ppm respectively (see Table 21), we conclude that average residues in milk will be 0.004 ppm, and average residues in the meat, fat and meat by-products (except liver) of cattle, goats, hogs, horses and sheep will be 0.010 ppm (0.020 ppm in liver). These values correct for 25% and 80% recovery for liver and other meat, fat and meat by-products respectively; and include 20% residues in addition to the values for G-28273 shown in the Tables to account for residues of atrazine and other chlorometabolites which were not found at detectable levels (estimation based on relative proportions of metabolites seen in ruminant metabolism studies).

Table 22: Residues of G-28273 in Cattle Tissues

	Maximum Residue (ppm)		
Tissue / Feeding Level --->	3.75	11.25	37.5
Loin	0.02	0.033	0.088
Round	<0.01	0.060	0.102
Omental fat	<0.01	<0.01	0.022
Perirenal fat	<0.01	0.012	0.020
Liver	<0.04	0.025	0.115
Kidney	0.014	0.031	0.087
Blood	<0.01	0.013	0.037

Table 23: Residues of G-28273 in Cow's Milk

	Maximum Residue (ppm)		
Day / Feeding Level --->	3.75	11.25	37.5
0	<0.01	<0.01	<0.01
1	0.02	0.09	0.39
2	0.02	0.08	0.28
7	0.03	0.08	0.33
12	0.03	0.12	0.46
19	<0.01	0.04	0.25
26	0.01	0.04	0.24

Laying hens were fed atrazine in their diets for 28 days at levels of 0, 0.5, 1.5 and 5.0 ppm (refs. 47, 48). Three chickens in each treatment group were sacrificed at 7, 14, 21 and 28 days after initiation of dosing, and tissue samples were obtained. Eggs were collected rom hens in each treatment group on days 0, 1, 3, 7, 10, 14, 17, 21, 24 and 28. No detectable residues were found in any tissue or eggs at the 0.5 ppm dosing level (LOD = 0.05 ppm for atrazine and each metabolite in liver, 0.01 ppm in other tissues). No residues of atrazine, G-30033 or G-28279 were found in any tissue at any dosing level. Residue data for G-28273 are summarized in Tables 24 and 25.

Table 24: Residues of G-28273 in Chicken Tissues

Tissue	Feeding Level --->	Maximum Residue (ppm)		
		0.5	1.5	5.0
Skin		<0.01	<0.01	0.02
Fat		<0.01	<0.01	<0.01
Liver		<0.05	<0.05	<0.05
Breast/thigh		<0.01	<0.01	0.03

Table 25: Residues of G-28273 in Chicken Eggs

Day	Feeding Level --->	Maximum Residue (ppm)		
		0.5	1.5	5.0
Pre		<0.01	<0.01	<0.01
1		<0.01	<0.01	0.01
3		<0.01	<0.01	0.04
7		<0.01	0.01	0.06
10		<0.01	0.01	0.06
14		<0.01	0.01	0.05
17		<0.01	0.01	0.06
21		<0.01	0.01	0.07
24		<0.01	<0.01	0.05
28		<0.01	<0.01	0.05

Based on these data, we conclude that the average combined residue of atrazine and its chlorometabolites likely to be found in eggs or in the meat, fat and meat by-products of poultry resulting from registered applications of the herbicide to animal feeds is far less than the limit of detection for the analytical method. It is, therefore, unlikely that any significant residues will be contributed to the human diet from these sources.

Attachments (2): Bibliography, Confidential Appendix
cc with attachment: M. Metzger (DEB), Atrazine S.F., TOX, R.F.,
E. Eldredge (ISB/PMSD), PM#25, SACB
cc without attachments:Circu (7)
RDI:E.Zager:EZ:9/6/88:RDS:9/6/88
TS-769C:DEB:M.Metzger:MM:Rm803a:CM#2:9/6/88

Attachment 1

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Attachment 2

Confidential Appendix

Atrazine

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