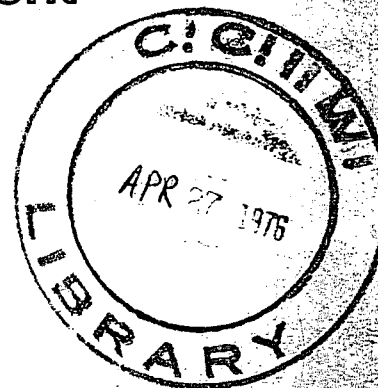**Environment Canada**

Environnement Canada

Canada Centre For Inland Waters

Centre Canadien Des Eaux Intérieures

ATRAZINE

Toxicity, Use and Persistence

by the

CCIW Toxic Substances Group

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Properties

Atrazine is the common name for 2-chloro-4-ethylamino-6-iso-propylamino-s-triazine. Its basic chemical structure is the symmetrical triazine ring, which also forms part of a number of similar compounds, such as simazine, cyanazine, cyprazine and metribuzin. Its chemical structure is
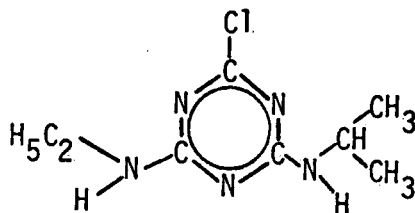
with a mol. wt. MW 215 and the formula $C_8 H_{14} N_5 Cl$. The pure compound has a melting point of 173-175°. Its solubility in water decreases from 70 mg/ℓ at 25°C to 22 mg/ℓ at 0°C. It is readily soluble in common organic solvents.

At present, atrazine is neither manufactured nor formulated in Canada. It is all imported from the United States and other countries, and is, in some cases, packaged here. The patent for manufacture, held by Ciba Geigy Co., expires in about a year in Canada. The Canadian market is reportedly not large enough to justify a production facility in this country.

Use

Atrazine is a pre-emergent herbicide. More than 95 percent of the atrazine consumed in Canada is used on corn crops for weed control,

and greater than 90 percent of this is used in Ontario and Quebec. The remaining 5 percent is used as a soil sterilant in industrial areas, notably in petroleum storage compounds to reduce the fire hazard posed by vegetation. It is also used on railroad beds to prevent weed growth which would otherwise inhibit the drainage of ballast under the ties.

Statistics Canada reports atrazine usage in a basket category entitled "Other selective post-emergent herbicides". Also included in this total are barban, Stam-F, solan, endothall, dicamba, dicamba-phenoxy mixtures, bromoxynil, and bromoxynil-phenoxy mixtures. In 1973, the national consumption figure for this category was 1,728,978 kg. valued in excess of thirteen million dollars. Provincial breakdowns are unavailable due to confidentiality restraints.

Data on atrazine usage in Ontario in 1973 have been assembled under Task B-4 of PLUARG. A condensation of these data is presented by county in Table 1. Total usage in Ontario for 1973 was 934,687 kg. Of this total, 33 percent was applied as pure material, 42 percent was applied as atrazine plus oil, etc., and 25 percent was applied in mixtures with other herbicides (Bladex, Lasso, Sutan, linuron).

To determine the approximate amount of atrazine used in each lake basin in 1973, the consumption figures for the counties have been multiplied by the percentage of farmland of the counties that lie within each basin (Table 2). Greater than 99 percent of all the atrazine used in Ontario in 1973 was applied to land in the Great Lakes Basin: 60 percent in the Lake Erie Basin, 26 percent in the Lake Huron Basin, and

TABLE 1

USE OF ATRAZINE IN ONTARIO BY COUNTY, 1973 (kg.)

County	In Mixtures	Atrazine plus oil, etc.	Atrazine, Pure	Total
Brant	13,225	6,221	7,823	27,269
Bruce	4,800	10,717	13,467	28,984
Dufferin	2,790	875	2,417	6,082
Durham	3,821	7,474	2,429	13,724
Elgin	14,813	40,995	23,194	79,002
Essex	5,292	10,740	8,556	24,588
Frontenac	22	1,463	1,877	3,362
Grey	1,538	4,081	7,270	12,889
Haldimand	1,153	6,419	6,499	14,071
Halton	2,006	920	1,671	4,597
Hastings	2,835	4,764	2,896	10,495
Huron	12,348	41,110	30,060	83,518
Kent	20,364	50,266	36,059	106,689
Lambton	9,029	30,803	21,174	61,006
Lennox and Addington	302	5,369	676	6,347
Middlesex	28,365	45,545	18,096	92,006
Niagara	1,480	7,079	3,064	11,623
Norfolk	13,883	11,251	5,000	30,134
Northumberland	6,264	5,728	3,177	15,169
Ontario	6,559	4,164	5,536	16,259
Oxford	26,969	24,987	21,340	73,296
Peterborough	2,356	2,058	2,527	6,941
Perth	9,536	22,211	18,935	50,682
Peel	3,893	2,266	1,287	7,446

TABLE 1

USE OF ATRAZINE IN ONTARIO BY COUNTY, 1973 (kg.)-Cont'd

County	In Mixtures	Atrazine plus oil, etc.	Atrazine, Pure	Total
Prince Edward	2,063	4,013	2,530	8,606
Simcoe	9,955	13,042	8,863	31,860
Thunder Bay	–	–	–	–
Victoria	1,504	2,237	2,542	6,283
Waterloo	14,071	6,486	11,888	32,445
Wellington	5,981	9,494	21,474	36,949
Wentworth	3,122	6,224	5,450	14,796
York	3,436	7,926	6,207	17,569
TOTAL	233,775	396,928	303,984	934,687

Source: Condensed from Task B, Activity 4, PLUARG

5.

TABLE 2

USE OF ATRIZINE BY LAKE BASIN, 1973 (kg)

County	Lake Erie	Lake Ontario	Lake Huron	Lake Superior	Total
Brant	27,269	–	–	–	27,269
Bruce	–	–	28,984	–	28,984
Dufferin	3,102	486	2,494	–	6,082
Durham	–	13,724	–	–	13,724
Elgin	79,002	–	–	–	79,002
Essex	24,588	–	–	–	24,588
Frontenac	–	1,109	–	–	1,109
Grey	129	–	12,760	–	12,889
Haldimand	10,553	3,518	–	–	14,071
Halton	46	4,551	–	–	4,597
Hastings	–	9,655	–	–	9,655
Huron	1,670	–	81,848	–	83,518
Kent	106,689	–	–	–	106,689
Lambton	45,144	–	15,862	–	61,006
Lennox and Addington	–	6,284	–	–	6,284
Middlesex	68,084	–	23,922	–	92,006
Niagara	1,162	10,461	–	–	11,623
Norfolk	30,134	–	–	–	30,134
Northumberland	–	15,169	–	–	15,169
Ontario	–	7,642	8,617	–	16,259
Oxford	73,296	–	–	–	73,296
Peel	–	7,372	74	–	7,446
Perth	33,957	–	16,725	–	50,682
Peterborough	–	6,941	–	–	6,941
Prince Edward	–	8,606	–	–	8,606

TABLE 2

USE OF ATRIZINE BY LAKE BASIN, 1973 (kg)-Cont'd

County	Lake Erie	Lake Ontario	Lake Huron	Lake Superior	Total
Simcoe	–	191	31,669	–	31,860
Thunder Bay	–	–	–	–	–
Victoria	–	5,529	754	–	6,283
Waterloo	32,445	–	–	–	32,445
Wellington	26,234	2,586	8,129	–	36,949
Wentworth	–	10,653	4,143	–	14,796
York	–	10,014	7,555	–	17,569
TOTAL	563,504	124,491	243,536	–	931,531

13 percent in the Lake Ontario Basin. Note that these figures are approximate, having been used on total farmland (not just corn) in use in the mid-1960's.

Analysis

Atrazine, together with other triazine herbicides and a number of degradation products is extracted from water with ethyl acetate (Beynon, 1972), the procedure has been refined by Ripley et al. (1974). Concentrated extracts can be directly measured after gas liquid chromatography on Carbowax 20 M and other stationary phases with sensitive detectors (alkali flame, electron capture detector or Hall electrolytic conductivity detector). Sherma (1973) reported sensitivity limits for atrazine of 1 μg/ℓ in water and 0.02 μg/g in soil. A method reported by Junk et al. (1975) applies XAD-2 resin in 2 g quantities for the extraction of 100 ℓ water samples. This procedure proved very efficient and accurate; at concentrations of 0.02 μg/ℓ the average recovery of atrazine was 90 percent. Present routine quantification limits are approximately 0.01 μg/ℓ in water for atrazine, DEA (de-ethylated atrazine) and DIA (de-isopropylated atrazine), cyprazine and cyanazine (Muir and Baker, 1976).

Degradation

The degradation of atrazine results in the first step in compounds in which the triazine structure is retained. Three major deriv-

atives, commonly observed are:
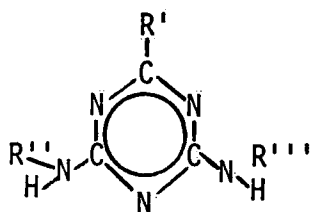
R'	R''	R'''	
OH	C_2H_5	C_3H_7	Hydroxy-atrazine
Cl	H	C_3H_7	DEA
Cl	C_2H_5	H	DIA

DEA and DIA appear to be the predominant atrazine degradation products in soils. Both Beynon et al. (1972) and Muir and Baker (1976) report these compounds at approximately twice the level of the parent compound atrazine in upper levels of soil and in tile-drain water from fields treated with atrazine.

Biological degradation of atrazine apparently occurs either via substitution of the chlorine atom with hydroxyl (Skipper et al., 1967; Obien and Green, 1969) or via dealkylation of either or both of the two amine substituents (Kearney et al., 1965). The latter reaction apparently does not readily cleave the triazine ring and hence could be expected to result in metabolites of toxic concern. In aerated surface soil, the ring is cleaved subsequent to hydroxylation. In submerged sediments (Goswami and Green, 1971) it was demonstrated that atrazine was very slowly metabolized presumably due to the inability of these sediments to first hydroxylate the compound. It would also appear that rats can metabolize both the parent atrazine and its hydroxylated analogue (Bakke et al., 1972).

Numerous atrazine degrading microorganisms have been isolated and identified. Among them the bacteria (Arthrobacter, Bacillus, Pseudomonas) and fungi (Aspergillus, Cladosporium, Fusarium, Pencillium) have

been shown to utilize the compound as carbon, nitrogen and/or energy source.

(1) Dealkylation:

Dealkylation appears to be the major mechanism involved in the microbial degradation of atrazine. This mechanism does not necessarily insure detoxication. Dealkylation of atrazine resulted in the formation of DEA, DIA and 2-chloro-4,6-diamino-s-triazine which were almost as toxic to oats as the parent compound, atrazine.

(2) Hydroxylation:

Only one example is presently known where a soil microorganism, Fusarium roseum hydrolyzed the Chloro-S-triazine atrazine to it corresponding hydroxyatrazine.

(3) Ring cleavage:

Results with C^{14} -ring-labelled s-triazine indicate that the ring structure is somewhat resistant to microbial attack. Ring cleavage apparently occurs only after hydroxylation but the mechanism for the cleavage is not known. However, it seems likely that complete ring cleavage is not a major mechanism for degradation in soil.

(4) Conjugate formation:

Conjugate formation of atrazine with carbohydrates, amino acids or nucleoproteins has been demonstrated in a few reports. Not much is

known about the role of conjugate formation in the inactivation of s-triazines.

Movement and Persistence

Several publications refer to the movement and persistence of atrazine in soils and water. The occurrence of atrazine and its degradation products in surface waters is a result of its precipitation into waterways from the air, from surface runoff and from soil leachates. The latter two modes of entry must be considered as major pathways.

Direct surface runoff contribution is affected by the soil and terrain (Ritter et al., 1974) and by climatic conditions. Hall et al. (1972) and Hall (1974) reported the presence of atrazine in runoff water up to 12 months after a single application. Muir and Baker (1976) studied the concentration of several triazine herbicides and their degradation products in tile-drain water over a period of 18 months, single field applications of atrazine, and other herbicides, in June of each of two successive years resulted in atrazine levels of 0.06 to 10.8 $\mu g/\ell$ with a mean of 0.95 $\mu g/\ell$. Both DEA and DIA were observed parallel to undegraded atrazine. In the same water samples, DEA ranged from 0.36 to 7.71 $\mu g/\ell$ (mean 1.12 $\mu g/\ell$) and DIA ranged from 0.01 to 0.78 $\mu g/\ell$ (mean 0.08 $\mu g/\ell$), obviously, DEA appears to be a major intermediate in the chemical and biological degradation of atrazine. In fact, of the 23 water samples analysed over the period of 1.5 years, in all but three samples had higher DEA than atrazine residues; the exceptions being those

shortly after the field applications. Remarkably, DEA levels by and large are constant (0.70 and 0.58 µg/ℓ, respectively) about one year after the applications of atrazine.

Given the definition of a persistent pesticide as: "A persistent compound is defined as one which by itself or as its transformation product, has a halflife for degradation under natural environmental conditions of more than eight weeks" (IJC, 1975), one might have to regard atrazine as environmentally persistent. However, it should be borne in mind, that further chemical and biochemical degradation of DEA is likely to proceed more quickly under lentic conditions relative to the apparently slow degradation in soil.

Hall et al. (1972) reported annual losses of atrazine to runoff water and sediment from a single application as a few percent of the applied load. The same study indicated 68, 21 and 16% of the atrazine remaining as such in the soil after 1, 3 and 12 months respectively. Atrazine and other triazines were also identified in finished New Orleans drinking water at levels of 0.2 to 5 µg/ℓ by Keith et al. (1975). Junk et al. (1975) reported atrazine levels of 0.2 to 0.42 µg/ℓ in surface waters of an Ohio agricultural area.

In a study of several creeks in the corn growing areas of southern Ontario, atrazine levels of up to 0.8 µg/ℓ were observed in November, presumably several months after the field application (Hodson, 1976). Various ecosystem compartments sampled at the same time, did not show any atrazine residues above the quantification limit (0.01 µg/g). This sampling program was repeated in the following June (1975), when

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atrazine applications were presumably high. Atrazine levels in the runoff water rose above 1.0 µg/ℓ and reached 14.6 µg/ℓ at one site (Little Ausable R., Huron County). Corresponding residue levels in other parts of that ecosystem in µg/g were: clams, 0.082; shiners, 0.056; suckers, 0.028; and shad, 0.16 µg/g, respectively.

Toxicity

Of 18 species of marine unicellular algae, Walsh and Hollister (1973) found atrazine less toxic than several other herbicides tested. However, wide variations occurred in response to the toxicants, even among the individual species of the same family. It is therefore necessary, for algal bioassays to use several species from each of several families in order to obtain realistic data on the toxic effects of such herbicides. Table 3 gives data on atrazine concentrations and their effects on algae growth and oxygen evolution (Hollister and Walsh, 1973). Similar effects of atrazine were observed on freshwater algae by Hiranpradit (1975).

TABLE 3

Concentrations of technical atrazine in mg/ℓ that decreased oxygen evolution or growth of algae by 50% (EC_{50}) and 100% (EC_{100}); (Hollister and Walsh, 1973).

Algae Species	Oxygen		Growth	
	EC_{50}	EC_{100}	EC_{50}	EC_{100}
Chlorococcum sp	0.10	0.40	0.10	0.50
Dunaliella tertiolecta	0.30	0.70	0.30	1.20
Isochrysis galbana	0.10	0.20	0.10	0.20
Phaeodactylum tricornutum	0.10	0.20	0.20	0.50

For freshwater organisms, atrazine is recorded to be acutely toxic (TL_m) at 3600 µg/ℓ to <u>Daphnia</u> <u>magna</u> and at 12600 µg/ℓ to rainbow trout, determined in static tests by Sunshine (1969). Shcherban (1973) reported decreased fertility of <u>Daphnia</u> <u>magna</u> at 100 µg/ℓ atrazine.

For rats, Metcalf (1971) found the acute dose (LD50) of atrazine in excess of 3080 µg/kg body weight. A chronic toxicity study by Gysin and Knulsi (1960) did not observe toxic effects of atrazine at a dietary level of 100 µg/g for rats over a period of two years.

The toxicity of degradation products of atrazine is not sufficiently investigated. In general, it can be assumed that all derivatives with an uncleared s-triazine ring, such as DEA and DIA exhibit similar toxic effects as the parent compound atrazine.

Environmental levels

Limited surveys on residual atrazine in water samples are reported in the literature. Table 4 gives a compilation of some of the pertinent data for surface waters of Quebec, Ontario, and for some US watersheds.

In addition to above data on water samples from field locations, atrazine has been reported in sediments, clams and fishes from Ontario (Hadson, 1976). A survey by Thomas and Frank (1976) on sediments of approximately fifty rivers and creeks in southern Ontario observed atrazine only rarely above the detection limit of 0.05 µg/g. A maximum level of 1.1 µg/g atrazine was found in a sediment sample from Thirty-Mile Creek.

TABLE 4

Location	Atrazine, concentration in µg/ℓ		Sampling Date	Reference
	range	mean		
Quebec				
R. St. Nazaire	0.02 - 26.9		May - Dec.	Baker (1976)
R. Chibouet	0.02 - 9.5		April - Dec.	"
R. Salvail	0.02 - 10.6		April - Dec.	"
Ontario				
C. Creek (Wellington C.)	0.3	---	Nov. 1974	Hodson (1976)
Big Creek (Essex C.)	0.8	---	Nov. 1974	"
Hillman Creek (Essex C.)	0.3	---	Nov. 1974	"
"	2.6 - 3.3	3.0	June 1975	"
Little Ausable (Huron C.)	0.4	---	Nov. 1974	"
"	14.0 - 14.6	14.3	June 1975	"
Creek, Thames (Oxford C.)	0.1	---	Nov. 1974	"
"	0.8 - 0.9	0.8	June 1975	"
Skunk Creek (Grey C.)	0.4	---	Nov. 1974	"
"	0.3	---	June 1975	"
Creek, Vineland (Niagara C.)	0.2	---	June 1975	"
Iowa				
Several rivers	0.05 - 42.0	---	June-Aug. 1974	Junk et al. (1975)
Louisiana				
Mississippi R.	1.2	---	July 1974	Junk et al. (1975)

As mentioned above, atrazine readily degrades to hydroxy-atrazine, DEA and DIA, at least under favourable conditions. It can therefore be assumed, that DEA, a major metabolite of atrazine, might be observed in many water sediment and biota samples at higher levels than atrazine itself. Apparently, no field sampling has been designed in this respect.

Conclusions

1. In Ontario, the consumption of atrazine is approximately 1,000,000 kg per year. About 50% of that is applied on corn fields in the Lake Erie watershed.

2. Under certain conditions, atrazine is rapidly degraded to hydroxy-atrazine and to de-ethylated and de-isopropylated forms. Some of these compounds appear to be more stable than atrazine.

3. Atrazine concentrations of less than 100 µg/ℓ reduce significantly the growth and oxygen evolution of some algae and decrease the reproduction of Daphnia magna. The toxicity of atrazine metabolites and degradation products is not known.

4. Atrazine concentrations in surface waters, following field application were found as high as 15 µg/ℓ in Ontario and up to 27 µg in rivers in Quebec.

5. Atrazine does not appear to be bioconcentrated, however it may be quite persistent under anoxic conditions.

6. Great Lakes' waters, particularly those of Lakes Erie and
   Huron ~~are likely to~~ **might** become contaminated with atrazine in
   certain nearshore areas during the prime months for atrazine
   use (June to August).

7. Any monitoring of Great Lakes waters should restrict itself
   to these months and to nearshore and rivermouth areas.

8. Any monitoring of atrazine should be accompanied by the meas-
   urement of de-ethylated atrazine.

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