

To : Randy Segawa, Sr. Env. Res. Scientist  
Env. Hazards Assessment Program

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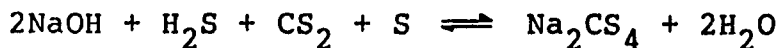
Judy Pino, Env. Research Scientist  
Environmental Hazards Assessment Program

Subject: Literature Review of the Environmental Fate of Sodium Tetrathio-  
carbonate (Enzone)

This review is based on data from the CDFA pesticide registration packages submitted by Unocal Corp (51031-001 through 51031-037), referenced herein as U-0xx; and on literature located through searches of SciSearch (1974-90), Analytical Abstracts (1980-90), Biosis (1969- 90), CAB Abstracts (1972-90), Agricola (1979-90), and Chem Abstracts (1967-90), referenced by author.

### Introduction

Enzone (sodium tetrathiocarbonate, sodium perthiocarbonate, or GY-81) is a post-plant nematicide, soil insecticide, and soil fumigant. It is marketed as an aqueous ready-to-use solution produced by the equilibrium reaction (U-021):



Enzone is designed as a stable, non-flammable source of carbon disulfide, a decomposition product of the rapid hydrolysis of the tetrathiocarbonate anion (TTC) under soil conditions. Carbon disulfide was the first reported soil fumigant; it was used in Europe during the 1870's to control the sugar beet nematode (Young and Green 1988; Matheron and Matejka 1988; Gallian and Hafez 1984). However, its volatility, high liquid and vapor toxicity, and extreme flammability have made its direct use impractical.

Enzone can be applied to the soil either prior to planting or after plant growth is established. Application methods include drip and low-volume sprinklers and emitters, flood and furrow irrigation, and shank application. Normal application rates are 5-60 gallons/acre with 100 gallons/acre/year maximum. In 1989 Unocal received an Experimental Use Permit for 280,265 gallons of Enzone for the treatment of 4,000 acres of crops in the US, including 3,250 acres in California (U-039; Robison 1989; Matheron and Matejka 1987).

Enzone is currently applied in the spring and fall to grapes, oranges and grapefruit, and in the fall to potatoes, for control of plant parasitic nematodes and Phytophthora root rot in citrus.

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Unocal is evaluating its prospective use on almonds, peaches, apricots, avocados, cherries, walnuts, and other perennials. They plan to include annual crops such as cotton, and tomatoes in future research.

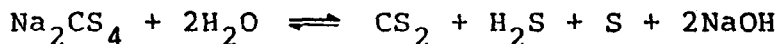
Physicochemical Properties of Tetrathiocarbonate

Molecular Weight	186 g mol <sup>-1</sup>
Specific Gravity	1.26 with reference to water at 25 °C (U-021)
Vapor Pressure	25 mm Hg, 25 °C (U-021) (VP for CS <sub>2</sub> = 362 mm Hg, 25 °C (Dean 1973))
Hydrolysis Half-Life	1.5 hrs at pH 5 and 5000 mg L <sup>-1</sup> initial concentration (U-022) 25 hrs at pH 10 and 10,000 mg L <sup>-1</sup> initial concentration
Henry's Law Constant	N/A (inorganic highly polar salt in solution; however, for CS <sub>2</sub> , H = 1.1x10 <sup>-2</sup> atm m <sup>3</sup> g mol <sup>-1</sup> (U-021))
Kow	N/A (TTC is a highly polar, inorganic salt in solution)
Soil Adsorption Coefficient (U-021)	

Sand	Soil Type		Organic Matter	K (cm g <sup>-1</sup> )
	Silt	Clay		
90%	8.6%	1.4%	0.3%	0.43
88	7.6	4.4	0.3	0.61

**Soil Metabolism and Transport**

Tetrathiocarbonate moves into the soil with water and readily dissociates, by dilution or hydrolysis, into its constituent components, achieving its fumigation function (Young and Green 1988):



TTC's efficacy depends upon this rapid hydrolysis to carbon disulfide, hydrogen sulfide, sodium hydroxide and sulfur; 90% degradation of TTC occurs within 1-28 hours, depending on the soil's biological activity (U-009). The decomposition products have a

higher vapor pressure than the parent compound. Soil particles rapidly bind and immobilize the sulfur ion and the  $H_2S$  components, leaving the weakly bound  $CS_2$  to migrate and act as a biocide;  $CS_2$  is the only mobile degradation component. The major dissipation pathways for the resultant  $CS_2$  are physical diffusion to the soil surface and subsequent release to the atmosphere, and conversion by biodegradation or catalytic oxidation to sulfate and carbonate anions (U-021; Robbins 1955).

In a model system designed to study movement of these decomposition products, the initial  $CS_2$  soil concentration maximized in 1-5 hours, after which it declined to zero (U-028). A smaller second flush was observed in 48-72 hours, with a half-life of 28 hours. Soil  $CS_2$  levels diminished with time and were nearly undetectable after 8 days. It is postulated that it is unlikely that appreciable amounts of tetrathiocarbonate anion would contaminate an aquifer by elution; if contamination did occur, it would probably be via gaseous diffusion of the  $CS_2$  degradation product (U-009; U-021).

In an anaerobic metabolism study conducted by Unocal, the rate of decline of  $CS_2$  followed first order reaction kinetics, with an average half-life of 109 days (U-021). Both sterilized and unsterilized soil samples had similar anaerobic half-lives; thus, carbon disulfide anaerobic losses were probably not due to soil metabolism processes. Under aerobic conditions, rate of decline of carbon disulfide was found to be an order of magnitude greater than under anaerobic conditions, ranging from 2-27 days, depending upon soil biological activity and moisture; accelerated degradation under aerobic conditions was thought to be due to increased microbial activity (U-009; U-021).

Unocal conducted a study at Brea, CA to determine the movement of TTC and its carbon disulfide decomposition product with water. TTC was applied by sprinkler to columns of four soil types: sandy loam, coarse agricultural sand, fine sand, and clay loam. Air samples were collected at 1-, 3-, 5-, 7-, and 9-foot soil depths. TTC was found to move with water under saturated flow conditions with an  $R_f$  value of 0.5-0.7. TTC partition coefficients ranged from 0.31 in sand to 0.91 in clay loam (U-009; U-021). These high  $R_f$  values raised suspicions that TTC might be a potential groundwater contaminant; however, it was found that it will probably not move to depths below 40 cm in saturated flow under normal use conditions. As the TTC decomposes the released  $CS_2$  may diffuse to lower depths but will probably be somewhat restricted by its lability to oxidation. TTC's toxic constituents, hydrogen sulfide and carbon disulfide, have short lifetimes in the soil and thus probably short environmental persistence (U-001; U-010).

The fate of the other degradation products has been previously studied (Tisdale 1975): Elemental sulfur acts as a plant nutrient source, modifies the soil's cation content, and helps to maintain optimal pH. The hydroxyl moiety is neutralized on the soil surface or displaced, e.g., as insoluble  $Al(OH)_3$  (U-009).

### Groundwater

Unocal conducted a study to monitor  $CS_2$  residue impact on groundwater (U-021; U-026). Eight monitoring wells containing soil gas probes were installed in loamy sand soil. The site was flooded with 100 gal/acre TTC and the  $CS_2$  degradate was sampled.  $CS_2$  residues were detected only in on-site wells; maximum concentrations were reached within one day at a depth of one foot. The time required for  $CS_2$  to reach its maximum soil concentration increased proportionately with depth. After the maximum, declines were approximately exponential (first order in  $CS_2$  concentration). Soil gas  $CS_2$  half-lives ranged from 0.8-2.8 days. No measurable  $CS_2$  residues due to TTC application were detected in off-site wells or in groundwater samples monitored during the 49-day testing period, suggesting that lateral and horizontal movement are slow. Carbon disulfide transport in the soil probably occurs by gaseous diffusion rather than by leaching.

Two studies investigated the movement of  $CS_2$  in shallow aquifers. At Bradenton, Florida 200 gallons/acre were shanked 8" into soil with a water table at 18" and the plot was tarped. The maximum  $CS_2$  concentration reached was ~200 ppb at 24 hours; this had returned to a background level of ~25 ppb at four days (see Table I) (U-027; U-028).

A model system consisting of a soil column and a water table at 24" was reported in U-028. Experiments modelling a TTC application rate of 200 gal/acre showed a maximum of 97 ppb at six days with a return to background levels at 12 days (see Table II).

### Hydrolysis

Hydrolysis is a significant degradation route for TTC (U-022):

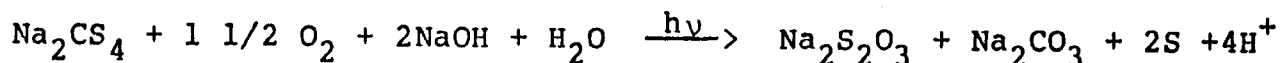


Hydrolysis is rapid at pH <9 with an apparent half-life of <2 hours. Dilution of tetrathiocarbonate solutions proportionately accelerates rate of hydrolysis with a corresponding decrease in lifetime (U-021). At low concentrations and under more acidic conditions, hydrolysis is essentially instantaneous; the apparent hydrolysis rate is indistinguishable from the rate of  $CS_2$  mass transfer from aqueous solution.

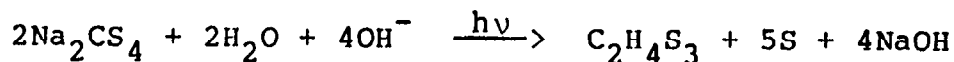
Rate constants decrease at pH >8 yielding half-lives of ~3-25 hours (U-022). At pH 10 and an initial Enzone concentration of 10,000 mg/L, TTC has a half-life of 25 hours. At pH 5 and an initial Enzone concentration of 500 mg/L, TTC half-life decreases to 66 minutes (see Table III).

### Photodegradation

Kinetic photolysis studies were conducted by Unocal (U-021; U-023). Dilute concentrations (0.47 to 1.69%) of Enzone in buffered distilled water were irradiated with a quartz mercury vapor lamp as an artificial sunlight source (total radiated energy 2.1 watts cm<sup>-2</sup>). Samples were periodically withdrawn to determine the disappearance of the TTC anion. At low concentrations, TTC readily undergoes photochemical catalysis to thiosulfate, carbonate and elemental sulfur and is thus unstable in water. The primary oxidative reaction is:



A secondary reaction, in which TTC is hydrogenated yielding 1,2,4-trithiolane (C<sub>2</sub>H<sub>4</sub>S<sub>3</sub>) and sulfur, also occurs under irradiation:



The major products of the two photolysis reactions include 48.52% thiosulfate, 33.57% elemental sulfur, 11.72% trithiolane, and 5.51% carbonate. TTC half-life ranged from 178 minutes (lowest initial concentration) to 1913 minutes (highest concentration) (U-021; U-023).

### Air Concentrations

Air monitoring studies were conducted during typical furrow-irrigation applications of TTC (at ~700 ppm; 25 gal/acre). No measurable quantities of the compound's degradation products, carbon disulfide (0.4 ppm limit of detection) and hydrogen sulfide (0.13 ppm limit of detection), were found above the furrows over a 24-hour monitoring period. In closed systems, e.g. drip irrigation, volatile losses will be minimized (U-011; U-020; U-021).

In a second study, air concentrations of CS<sub>2</sub> and H<sub>2</sub>S were monitored during tank filling, tractor driving and clean-up field operations when TTC was applied by shank injection. Carbon disulfide concentrations were <1 ppm, and no hydrogen sulfide was detected (U-011; U-021).

A series of air monitoring studies of the two potentially volatile degradation products of TTC, carbon disulfide and hydrogen sulfide, were conducted to determine suitable worker re-entry time (U-011; U-020; U-021). Vapor monitors were placed in three stations: on the treatment site, 50 ft. off-site in an upwind direction, and 50 ft. off-site downwind. Background CS<sub>2</sub> residues from the degradation of sulfur-containing organic matter were observed at an average level of 0.013 ppmv before treatment at various sites. Following chemigation applications of 100 gallons Enzone/acre, the highest CS<sub>2</sub> level detected in on-site monitors exposed during and for 8 hours after application was 1 ppmv, which was observed during a 10-minute period of the clean-up operation. The tractor driver's 8-hour time-weighted-average exposure was 0.62 ppm CS<sub>2</sub>. At a detection limit of 0.2 ppm, no hydrogen sulfide was observed before or after TTC application at any site.

#### Miscellaneous

Initial development of tetrathiocarbonate as a nematocide/fungicide candidate was undertaken with the ammonium and calcium salts. The initial EUP application was submitted for the more stable calcium tetrathiocarbonate to EPA in January 1984; a crop destruct EUP was initially granted followed by a non-destruct EUP. After experiencing field trial problems in 1984-5, Unocal changed Enzone's active ingredient from the calcium to the sodium salt. The results summarized above are drawn from studies involving either the calcium or sodium salt whose characteristics are stated to be similar (U-010).

Although TTC is toxic to fresh-water vertebrates and invertebrates (U-021), rapid aqueous degradation is believed to render it only slightly toxic to fish. It is believed that TTC should not pose a significant hazard due to the low probability of exposure and the low toxic potential (U-021).

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#### Attachments

cc: Ronald J. Oshima  
John Sanders

Table I

Analysis of CS<sub>2</sub> in Groundwater Samples at 18" Depth  
After Injection on Enzone and Tarping (U-028)

Treatment <sup>a</sup>	Replicate	Analysis on Day Number				
		0 <sup>b</sup>	1	2	4	8
Untreated	A	15*	7*	7*	7*	7
	B	12*	7*	7*	23*	13
	C	5*	20	41	16	20
	D	495	24	28	12	8*
100 gal/acre	A	17	40	11	12	72
	B	18	18	36	41	38
	C	190	9	23	17	7
	D	24	31	136	12	20
200 gal/acre	A	8*	191	20	10	6
	B	23	215	51	18	28
	C	5*	116	28	16	8
	D	48	119	33	16	8*

<sup>a</sup>All plots were covered with tarpaulins.

<sup>b</sup>Immediately before application.

\*Indicates detection limit for this measurement. Value of CS<sub>2</sub> concentration is less than this value. Confidence limits on all analyses are ±17% relative.



Table II

Movement of Enzone Decomposition Products in Soil  
Analysis of Model Water Table Results (U-028)

Measured CS<sub>2</sub> Concentrations (ng/mL)

Time (hours)	Upper Port <sup>1</sup>	Lower Port <sup>1</sup>
0	ND	0.82
1	ND	0.98
3	0.44	1.22
5	56	4.8
7	ND	3.2
24	ND	ND
27	0.28	0.92
31	0.26	0.78
48	0.53	0.76
55	ND	2.2
72	ND	6.8
144	40	97
168	9.4	0.8
192	ND	ND
216	8.6	16.2
240	13.2	10.4
312	7.8	6.2
342	2.4	6.8
360	6	4.6

<sup>1</sup>Upper and lower ports are 4 and 7 inches below the top of the water table.

Table III

Comparison of Rates of Disappearance of Enzone  
with Rates of Mass Transfer of CS<sub>2</sub> from Water (U-022)

[Enzone] mg/L	pH <sup>a</sup>	Rate Constant (min <sup>-1</sup> )	Half-Life (min)
500	5.4	0.0106	66
	7.0	0.0073	95
	9.4	0.0036	193
	8.0 <sup>b</sup>	0.0022	313
2000	5.6	0.0071	98
	7.1	0.0062	112
	9.6	0.0020	350
	9.6 <sup>b</sup>	0.0098	701
10000	4.9	0.0052	133
	6.9	0.0051	136
	9.9	0.0045	1510
	10.4 <sup>b</sup>	0.0060	1150

<sup>a</sup>Set with standard McIlvaine citrate-phosphate buffers.

<sup>b</sup>Number is the "autogenous" pH produced by dissolving Enzone at the specified concentration in deionized water.