Memorandum

To : Randall S. Segawa
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Date : November 14, 1990

Place : Sacramento

From : Department of Food and Agriculture — Wynetta S. Kollman, Assoc. Env. Res. Scientis
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Subject: Literature Review of the Environmental Fate of Chloropicrin

Chloropicrin (trichloronitromethane; nitrochloroform) is primarily used as a preplant soil fungicide to control root-attacking pathoger of high labor intensive crops such as strawberries and bell peppers, and as a soil fumigant for the control of nematodes, insects and wee seeds. It is also used as a fumigant for stored cereals and grains, and as a warning agent for use with odorless fumigants. During the first quarter of 1990 (January through March), total use of chloropicrin was more than 191,000 pounds. Of this amount, nearly 60% was used on strawberries and bell peppers (CDFA, 1990). Some physicochemical characteristics of chloropicrin based on accepted studies in registrant data packages (TriCal, 1987a; TriCal, 1987b; Chloropicrin Industry Panel, 1989) are listed below:

Physicochemical Characteristics of Chloropicrin

Molecular Weight	164.39 g/mole
Solubility	2000 ppm, 25 C
Vapor Pressure	23.2 mmHg, 25 C
Hydrolysis Half-life	354 days
Kh (Henry's Law Constant)	2.51E-03 atm.m /mol
Aerobic Soil Metabolism Half-life	0.374 days

Soil Adsorption:

Soil Type	Koc (cm /g)	Kd (cm /g)
Sand	91.0	0.273
Silty loam, 36%	2.52	0.139
Silty load, 28%	4.20	0.311
Sandy loam	3.65	0.263

Soil Transport and Metabolism

Chloropicrin, used singly or in combination with methyl bromide, is shank-injected 6 to 8 inches deep into moist soil for preplant soil fumigation. It rapidly diffuses in soil in all directions and kills

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target fungi within 9 to 24 hours (Wilhelm, 1987). To reduce the dissipation rate of gases into the air, the soil is automatically covered behind the shanks with polyethylene tarp simultaneously with injection.

Laboratory studies of a number of soils have shown that there is a high positive correlation between the percentage of clay or colloidal clay present in soil and the amount of chloropicrin adsorbed (Stark, 1948). It has also been shown that the amount adsorbed decreases with both increasing temperature (Stark, 1948; Tamagawa et al., 1985) and increasing soil moisture content.

Chloropicrin is degraded in soil by Pseudomonas sp. via a metabolic pathway involving three successive reductive dehalogenations to nitromethane: (Castro et al., 1983)

$$CCl_3NO_2 \text{---}> CHCl_2NO_2 \text{---}> CH_2ClNO_2 \text{---}> CH_3NO_2$$

Highly water soluble low molecular weight peptides are also produced by nonenzymatic reactions of chloropicrin with live or dead cells.

Laboratory aerobic soil metabolism studies on sandy loam soil (2.4% moisture, 12.96% organic matter, pH 5.7) showed a two-phase degradation mechanism with respective half-lifes of 0.042 and 0.374 days: A rapid initial degradation from the reaction of chloropicrin with living and dead organic matter followed by a slower microbial degradation that is affected by the diffusion rate of chloropicrin through soil (TriCal, 1987a).

Hydrolysis

A hydrolysis study as a function of pH was conducted to determine whether hydrolysis is a significant route of degradation (Chloropicrin Industry Panel, 1989). Chloropicrin (100 ppm) in aqueous buffered solutions at 25 C was found to be stable at pH 5, 7 and 9. During a 28 day period, no single hydrolytic product was formed at a level greater than 10%.

Photodegradation

The vapor-phase photolysis of chloropicrin was conducted by Moilanen et al. (1978) in the laboratory under simulated environmental conditions. Initial concentrations of 14.0, 1.4 and 0.01 g/ml were vaporized in a photoreactor and irradiated at sunlight wavelengths (>290 nm) for 70 days. For all concentrations, the half-life was 20 days with the photolysis rate slowing markedly thereafter. The initial photolysis products from the photochemical oxygenation of

chloropicrin followed by rearrangement and cleavage were phosgene and nitrosyl chloride:

$$CCl_3NO_2 \quad ---> \quad \underset{\text{Phosgene}}{COCl_2} \quad + \quad \underset{\text{Nitrosyl Chloride}}{NOCl}$$

Woodrow et al. (1983) conducted vapor-phase photolysis studies in the field after identifying phosgene and nitrosyl chloride as photolysis products in the laboratory. Chloropicrin was released into the field atmosphere along a broad front perpendicular to the prevailing wind. Drift samples were collected downwind from the application site with both high volume (1 m /min.) and low volume (28 L/min.) air samplers. The presence of phosgene in the field atmosphere was confirmed by trapping the compound as the carbonate in isobutyl alcohol.

Air Concentrations

Worker exposure studies have been conducted to determine air concentrations of chloropicrin during preplant soil fumigations by shallow injection (Maddy et al., 1984a; Maddy et al., 1984b). Occupational exposures for drivers and copilots are summarized in Table 1. The results varied widely from below the 1.0 ppb detection limit to 1,544 ppb. In both studies, drivers were exposed to the highest airborne levels with the highest and second highest values measured at 1,544 and 1,186 ppb (respective 120 and 127 minute sampling periods; 68.75 lb per acre application rate). The highest and second highest copilot exposures were 608 and 474 ppb (respective 127 and 120 sampling periods).

Airborne levels of chloropicrin 25 feet downwind during and after a preplant soil fumigation have been reported (Maddy et al. (1983). Air sampling was conducted in 45 minute periods at the rate of 0.2 LPM. Chloropicrin concentrations ranged from below the 1 ppb detection limit to 106 ppb, and increased after fumigation ended (Table 2). Maddy et al. (1984c) also measured airborne levels 50 feet downwind from 2 fumigation sites. Air was sampled in one-hour periods at the rate of 0.15 LPM at the first site, and in 2 hour periods at the rate of 0.075 LPM at the second. Chloropicrin concentrations at both sites fluctuated throughout the samplings periods, with levels ranging from below the 1 ppb detection limit to 81 ppb (Table 3).

Total hydrocarbon monitoring occurred in Watsonville, CA to determine ambient chloropicrin levels near residences adjacent to field fumigation activities (Fear, 1985). A 2:1 mixture of methyl bromide and chloropicrin (67 and 33%, respectively) was soil-injected to a depth of 12 inches at the rate of 350 lbs per acre. Using flame

ionization detection methods, total ambient hydrocarbon concentrations were monitored in one-hour sampling periods on a 24-hour continuous basis before, during and two days after fumigation. Elevated readings were detected during one application sampling period and three sampling periods occurring 20 hours after application. Assuming that chloropicrin and methyl bromide off-gas into the atmosphere at the same rate, these high chloropicrin concentrations were determined to be 0.233 ppm during application and 0.567, 0.733 and 0.400 ppm following application.

Ambient air monitoring for chloropicrin was conducted over a four week period during August and September of 1986 at three ambient locations in Monterey county, CA, and at an urban background site in the city of Monterey. Monitoring also occurred at a strawberry field application site south of Salinas before, during and 4 days after fumigation (Seiber et al., 1987). Two replicate samples were taken at each site with the exception of one ambient site, where three replicate samples were taken. Samples were collected on XAD-4 resin traps at a flow rate of 1 LPM for 4 hours and analyzed by a gas chromatogroaphic method with a 13 ppt detection limit. The results of the monitoring are summarized in Table 4. The highest chloropicrin concentrations were found at the field application sites and ranged from 110 to 23,800 ppm. Ambient concentrations ranged from below the detection limit at the background site to 681 ppm.

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Attachments

cc: Ronald J. Oshima
John Sanders

Table 1

OCCUPATIONAL EXPOSURES TO CHLOROPICRIN DURING PREPLANT SOIL FUMIGATIONS (SHALLOW INJECTION)

Study Site	Sampling Duration, Min.	Chloropicrin, ppb Driver	Chloropicrin, ppb Copilot	Air Temp., °F
		(Maddy et al., 1984a)[1]		
1	45	106	96	71
	45	47	26	74
	45	43	--[2]	74
	45	80	ND	82
2	45	126	181	67
		(Maddy et al., 1984b)[3]		
3	60	90	86	66
4	67	101	190	68
	64	154	178	72
5	127	1186	608	75
	120	1544	474	76
	60	244	116	75

[1] Application rate of 95.4 pounds per acre.
[2] Not detected, 1.0 ppb minimum detection limit.
[3] Application rate of 68.75 pounds per acre.

Table 2

AIRBORNE LEVELS OF CHLOROPICRIN DOWNWIND DURING AND AFTER PREPLANT SOIL FUMIGATIONS (SHALLOW INJECTION)

Maddy et al., 1983

	Chloropicrin, ppb		
Time	Site A	Site B	Site C
0900-0945	33	--	--
1015-1100	7	--	--
1115-1200	ND[a]	--	--
1400-1445	--	80	--
1500-1545	--	102	28
1600-1645	--	32	66
1700-1745	--	36	73
1800-1845	--	22	78
1900-1945	--	37	97
2000-2045	--	64	106
2100-2145	--	76	ND

a - None Detected. MDL = 1 ppb

Table 3

ADDITIONAL AIRBORNE LEVELS OF CHLOROPICRIN DOWNWIND DURING AND AFTER PREPLANT SOIL FUMIGATIONS (SHALLOW INJECTION)

Maddy et al., 1984c

	Chloropicrin, ppb				
Time	Site 1	Site 2	Site 3	Site 4	Site 5
Fumigation 1					
0700-0800	8	14	--	--	--
0800-0900	7	8	--	--	--
0900-1000	[a]ND	--	--	--	--
1000-1100	--	--	--	23	--
1100-1200	--	--	21	14	--
1200-1300	--	--	31	21	--
1300-1400	--	--	34	24	--
1400-1500	--	--	--	25	--
1500-1600	--	--	23	17	--
1600-1700	--	--	24	--	--
1700-1800	--	--	17	--	--
1800-1900	--	--	6	--	--
1900-2000	--	--	3	--	--
2000-2100	--	--	3	--	--
2100-2200	--	--	6	--	--
2200-2300	--	--	1	--	--
2300-2400	--	--	ND	--	--
2400-0100	--	--	11	--	--
0100-0200	--	--	2	--	--
0200-0300	--	--	--	--	81
0300-0400	--	--	--	--	31
0400-0500	--	--	--	--	32
0500-0600	--	--	--	--	44
0600-0700	--	--	--	--	23
0700-0800	--	--	--	--	17
0800-0900	--	--	--	--	7

Time	Site A	Site B	Site C
Fumigation 2			
0720-0920	16	--	--
0920-1120	15	--	--
1120-1320	16	33	--
1320-1520	13	30	--
0520-0720	40	18	--
0720-0920	--	--	20

a - None Detected. MDL = 1 ppb

Table 4

SUMMARY OF
AMBIENT AIR CONCENTRATIONS OF CHLOROPICRIN
IN MONTEREY COUNTY, CA

Parts per Million
(4-hour samples)

Location	Higest Positive[a]	Second Higest Positive[a]	Average of All Samples Above MDL	# Above MDL	Total # Samples Analyzed
Site 1	681	279	110	26	48
Site 2	57	23	40	4	46
Site 3	191	100	76	10	48
Site 4[b]	<MDL[c]	<MDL	<MDL	0	42
Field Application[d]					
Site A	730	110	170	12	22
Site B	9080	8100	1400	36	38
Site C	23800	3430	1970	32	36

a - Average of two replicates. Site 3 values are the average of three replicates.
b - Background site in the city of Monterey.
c - MDL=Minumum Detection Limit, 13 ppt.
d - Sites were located adjacent to a strawberry field.