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An Improperly Labeled Container with Chloropicrin: A Farmer's Nightmare

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An incident is described in which a Belgian farmer, following a successful tomato harvest period, purchased 400L of soil fumigant in two equal and similar containers, which were respectively labeled "Luxan Monam Concentré" and "Monam BASF". Both vessels were supposed to contain the same sterilant, "Monam®" (sodium methyldithiocarbamate, $CH_3.NH.CS.SNa$) in equal concentrations (510 g/L) as was indicated on their labels. Their contents were subsequently mixed in equal volumes in a 500 L tank and fumigated into a vegetable greenhouse at about 20 kg/acre through an automated inbuilt irrigation system. During the mixing stage, the farmer had put on a gas-mask (activated charcoal) and protective clothing, thus the acrid and toxic nature of the sterilant remained unnoticed.

Due to low velocity winds and dry weather conditions of that evening and the increased pressure in the greenhouse as a result of the fumigation, noxious fumes escaped through vents and were dissipated into neighbouring areas. The consequent hazards were observed when some 2,500 turkeys (fig. 1) in a run adjacent to the greenhouse, a substantial number of ducklings, 4 sheep and a goat were affected and died. The few surviving ducklings had visible signs of dyspnea and lacrimation, and exhibited a slow continued nodding of the head. They were unable to feed or move. A horse grazing near the scene was treated with antibiotics for fever, anorexia, repeated coughing, tonic spasm of the intercostal muscles and darkened mucosa. The surrounding vegetation was visibly discoloured. No fatal human casualties were reported, but a variety of physiological complaints, which included eye irritations, lacrimation, coughing, runny noses, nausea, sore throat, headache, dyspnea and skin irritations were registered amongst the local population within a 200-600m radius. These symptoms strongly suggested that a product other than Monam had been used, either in combination with it or alone. Apparently, one of the containers was filled with pure chloropicrin, which had been decanted into it without notice or change of label, while the other contained Monam, the desired material. Following the detection in air of the toxic material,

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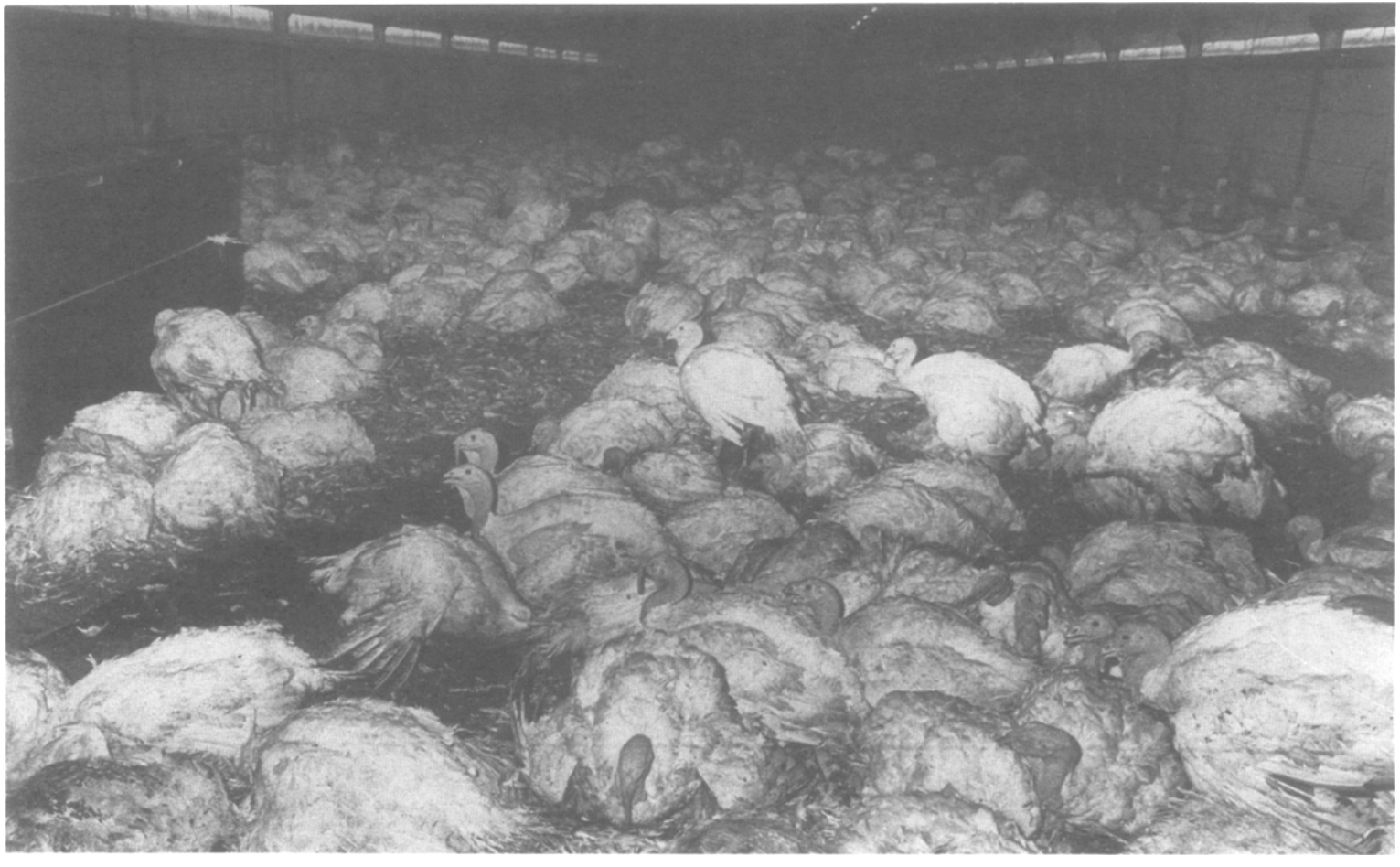

FIGURE 1. A fatal chloropicrin poisoning in turkeys.

the greenhouse was flooded with water and tarped and the residential area, albeit delays, evacuated.

A variety of samples from the scene was collected for analysis. They included: soil from the greenhouse, vegetables from the farmstore and area surrounding the greenhouse, the residual contents of both containers and the remains of a poisoned duckling. All samples were kept under refrigeration till time of analysis (1-4 weeks). The presence and identity of the responsible fumigant was confirmed by GC-methods. Its rate of dissipation from soil and plant material, and concentrations in different animal organs were determined. A clinical survey of the individuals initially exposed to the fumigant was also conducted. The results are presented and discussed below.

MATERIALS AND METHODS

Soil was collected in glass stoppered t-tubes and Erlenmeyer flasks. Vegetables were sampled in air-tight fruit jars.

n-Hexane (analytical grade) was subjected to GC-analysis and purified of interfering peaks by brief boiling (2 min.). Other attempts (Heikes and Hopper 1986) to purify this solvent were without success. The purified hexane was then spiked with 2,2,2-trichloroethanol (38.4 ng/ml) and re-analysed.

Undried soil, plant material and residual contents of the two fumigant containers were weighed into glass-stoppered vials each containing 5ml of extracting solvent(hexane). As for the analysis of sterilant in animal tissues, the brain, lungs, trachea, liver, kidney and fat tissue from the duckling were investigated. Each organ was weighed into a 10 ml aqueous protein precipitant solution containing 10% Na_2WO_4 acidified with 1N H_2SO_4. This was then extracted with 10ml of hexane. The resultant extracts were further centrifuged prior to GC analysis.

A Hewlett-Packard gas chromatograph HP 5890 equipped with an ECD (^{63}Ni electron capture detector) was used. Helium was used as carrier gas at a flow-rate of 20ml/min. A 30m x 0,53mm DB (Durabond) 624 fused silica capillary column (J&W Scientific Inc., Folsom, USA) was used. Chloropicrin concentrations were computed on a Trio Chromatography integrator (Trivector Inc., W. Chester). GC conditions were as follows: Detector/Injector temperature 300/230 °C; Initial/final temperature 90/200 °C; Initial/final time 4/10 min.; Rate 10 °C/min.

Fumigant standard: 93% pure chloropicrin(Chem Service Co., W. Chester) was used. Internal standard: 2,2,2-trichloroethanol (97%). The results obtained were corrected for the purity. Technical grade Monam (Standard) was kindly supplied by BASF(Belgium). A technical grade sample of chloropicrin was obtained from a local dealer.

RESULTS AND DISCUSSION

The results of the quantitative determination of the sterilant in various samples are summarized in table 1. The first two samples, A and B, were collected in the morning, 12 hrs after the incident had occurred. The relatively high concentrations of chloropicrin(average 20.9 ng/g), as

compared to samples C, D and E, which were sampled 4 weeks later, reflect the high dose (20 kg/acre) used in the sterilization process. Soils C, D and E were sampled at different depths. By this time, the greenhouse had been ventilated and the soil repeatedly churned-up. Sterilant levels in top(C) and mid soil(D) were thus drastically reduced (1.3 and 1.6 ng/g respectively).

Table 1. Sample, sampling times, weight extracted and concentrations of chloropicrin* obtained.

Sample	sampling time	weight extracted(g)	chloropicrin concentration(ng/g) found
I. Soil (greenhouse)			
A	12 hrs	4.74	18.8
B	12 hrs	4.00	22.4
C(0-10cm)	4 wks	5.34	1.3
D(30-40cm)	4 wks	5.40	1.6
E(40-50cm)	4 wks	5.00	4.0
II. Vegetables			
celery	3 days	2.37	3.6
spinach	2 wks	5.65	1.2
leek	2 wks	3.83	0.7
cabbage	2 wks	3.09	0.4
III. Animal organic material(Duckling).			
Brain	12 hrs	3.02	1.3
Trachea	12 hrs	1.72	15.0
Lungs	12 hrs	3.41	1.0
Liver	12 hrs	5.85	5.8
Kidney	12 hrs	5.07	1.6
Fat tissue	12 hrs	3.00	9.0
IV. Other.			
Monam BASF	12 hrs	0.0019	2000
Luxan Monam	12 hrs	1.0001	STRONGLY POSITIVE
Monam (standard)	---	1.2	NOT DETECTED.

* volume of solvent used in the extration: 5ml(I-III); 10ml(IV).

The rate of dissipation of chloropicrin in the soil is highest when the soil water content is reduced and decreases when this content is increased (Tamagawa 1985). Thus the significant residual concentration (4.0 ng/g) observed in the bottom soil (40-50cm) is due to both the high humidity and reduced aeration. Interestingly, the above mentioned chloropicrin concentrations do not appear to be phytogenic: a germination experiment with garden cress was carried out successfully. It was also observed that leek, though visibly affected, continued to grow.

A qualitative analysis 24 hrs after the incident of some vegetables and fruit collected from the farmstore and area surrounding the greenhouse indicated a strong contamination with chloropicrin. As a result, the farmer was dissuaded from consuming or selling his products. Quantita-

tive GC-analysis of some of these products (table 1) collected a few days later still showed a presence of chloropicrin, although at reduced levels. Celery, showing 3.6 ng/g chloropicrin, was collected 3 days after the incident. The rest were sampled 2 weeks later. Except for the spinach, which still indicated a relatively high chloropicrin presence, other plants indicated a significant reduction of contamination.

The persistent nodding by the few surviving ducklings indicated a poisoning of the CNS. The amount of fumigant found in the brain extract (1.3 ng/g) suggests that cerebral congestion had contributed to the death of the animals. Further confirmatory studies in this regard are necessary as no reports of chloropicrin neurotoxicity have appeared in the literature so far. One of the immediate targets in chloropicrin poisoning is the respiratory tract. Thus the relatively high concentration found in the trachea(15.0 ng/g) could be expected. Reasons for the low levels observed in the lungs are unclear. However a veterinarial pathological examination of a few poisoned turkeys revealed hemorrhagic diathesis of the lungs. Chloropicrin concentrations in the liver and kidney point to a breakdown process of this compound by the liver. This product also accumulates in the fat tissue (9 ng/g).

The two sterilants that were mixed and fumigated, "Luxan Monam Concentré" and "Monam BASF", were obtained as residues from their respective containers. Monam (Standard) was a gift from the manufacturer. Chloropicrin was absent in the standard but present in Monam BASF (2 µg/g). Contamination of the latter may have occurred during the preparatory step. The containers were probably rinsed one into the other during the mixing stage prior to the fumigation process.

35 people, mostly rescue workers(firemen, police, etc.) were among the seriously exposed and were admitted at a hospital emergency unit. Although they were medically examined at different times several hours after the exposure, 7 of them still showed an elevated level of methemoglobin (table 2).

Table 2. Duration of exposure and methemoglobin levels in seriously affected individuals.

Individual no.	Estimated duration of exposure(hr)	Methemoglobin level(% of Hb)** I.	II.
1.	8	11.7(5)	0.2***
2.	6	7.7(4)	0.7
3.	?	4.0(?)	0.6
4.	5	3.7(12)	-
5.	6	2.5(4)	0.7
6.	7	1.5(6)	0.2
7.	1	1.5(4)	1.5

** I. values between brackets indicate time in hrs of measurement of methemoglobin levels after cessation of exposure
II. methemoglobin levels 12hrs later than in I.
*** after treatment with O_2.

Chloropicrin, CCl_3NO_2 (syn. trichloronitromethane; nitrochloroform), is a known World War I chemical warfare agent. It is a colourless viscous liquid (b.p 112.4 °C) with a strong pungent odour. It is practically insoluble in water (0.2272 and 0.1621 g/100 ml H_2O at 0 °C and 25 °C respectively), is soluble in ether and is miscible with most organic solvents. Nowadays, this compound is mainly used as a pesticide (insects and rodents), soil fumigant and in organic synthesis (e.g. crystal violet). It is a potent lacrimator, skin and pulmonary irritant capable of eliciting nausea, coughing, vomiting, colic and diarrhoea, if ingested (Sutton 1963). Its LD_{50} in mice is 250 mg/kg (Chem Service Inc. 1987). In Belgium, this product is mainly imported for use in agriculture as a soil sterilant and its application is restricted to licensed commercial applicators.

Monam® (sodium methyldithiocarbamate, $CH_3.NH.CS.SNa$) has an odour similar to that of carbon disulfide. In contrast with chloropicrin, this product is soluble in water (72.2 g/100ml H_2O at 20 °C) and is sparingly soluble in most organic solvents. Concentrated aqueous solutions of this product are stable, with decomposition only occurring when in dilute solutions or in the presence of acids and heavy metals (Stechner 1968). It may also cause irritations to the skin and mucous membranes but has no reported lacrimatory properties. Its oral LD_{50}(mice) is 285 mg/kg (Stecher 1968). Following the detection of the noxious gas, the greenhouse was flooded with water and tarped (plastic sheeting) to prevent further dissipation of the sterilant into the environment. In this manner, the fumigated Monam was diluted leading to its decomposition. Chloropicrin, on the other hand was trapped.

Although there has been ample human experience with chloropicrin because of its use as a war gas, published reports involving intoxications and analysis in humans are scanty. Data on the effects of exposure to this compound are largely drawn from World War I findings. Concentrations of 0.8 and 2.0 mg/L for a duration of exposure of 30 and 10 minutes respectively have been reported lethal. Death usually results from pulmonary edema. The lowest irritant concentration is 0.009 mg/L and intolerable levels range between 0.05 and 0.1 mg/L (Sutton 1963). From the clinical findings above, the concentration of chloropicrin that had dissipated into the environment was estimated between 0.1 and 0.05 mg/L. Intoxication at these concentrations largely depends on individual sensitivity. Although there is a decrease in methemoglobin levels with time(Table 2), no clear time-concentration relationship could be drawn. The prescribed safety margin for this compound is 0.7 mg/m^3(0.1 ppm) (Hayes 1975; Proctor and Huges 1978; Parmeggiani 1983).

Judging from the foregoing analysis, the two containers certainly contained different sterilants. Although both were destined to contain Monam, the one labeled "Luxan Monam Concentré" apparently contained pure chloropicrin. This material had been erroneously decanted into an empty container with this label without notice. This fatal mistake either occurred at the chemical plant, harbour or distributing agent. The second vessel had the desired fumigant (Monam) but became contaminated during the mixing process.

Chloropicrin is usually fumigated at about 8 kg/acre, while Monam may be fumigated at 20 kg/acre. Since concentrated solutions of the lat-

ter are stable, it is relatively simple to administer and can be safely handled by any sufficiently experienced or trained farmer. The farmer had sufficient experience with this material, which in Belgium is sold as a water soluble concentrate (510 g/L sodium methyldithiocarbamate) and not in combination with chloropicrin (Kidd et al 1986). The fumigation method as used by the farmer was standard.

Sterilization using chloropicrin on the other hand, requires appropriate equipment, methodology and specially trained personnel. Due to the high dose of chloropicrin used and the faulty method of application, this fumigant escaped through vents in the greenhouse and was slowly spread by the low velocity winds to neighbouring areas. Chloropicrin vapour is invisible, heavier than air and spreads along the ground (Heikes and Hopper 1986). Hence the dissipation of this compound following the fumigation process was very slow. Its long persistence in the poultry-run and over the grazing field was an additional factor responsible for the loss of animal life observed.

The toxicity of chloropicrin has not been clearly elucidated. Apparently, damage is not only produced to the respiratory system, but also to the liver, kidneys, and central nervous system. No significant reports on chronic or systemic cases of poisoning in human beings have been recorded. A periodic medical examination of workers repeatedly exposed to low concentrations of this compound is recommended (Parmeggianni 1983). However, the effect of such repeated small doses has not been determined. Treatment of chloropicrin poisoning is largely technical (first aid) and involves administration of oxygen by mask or cannula and washing with large amounts of water in the case of eye and skin irritations (Proctor and Huges 1978). No specific treatment or antidote is known for chronic effects. In the light of the foregoing, we recommend that this product be replaced by less toxic and more laboratory evaluated sterilants.

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