fatty acids with iodine vapor and used 2',7'-dichlorofluorescein thereafter. The error induced by iodine has been noted by others (Nichaman et al., 1963). Also, the presence of small quantities of water from the silica gel HR layer interfered with the boron trifluoride procedure (Metcalf et al., 1966) for methyl ester preparation. The potential problem was overcome by resorting to transmethylation with H_2SO_4 in methanol (Boatman et al., 1969).

The fatty acid composition of the individual phospholipids in barley (Tables II and III) was similar to that in corn (Weber, 1970). Linoleic acid (18:2) was the predominant fatty acid in six fractions, PC, LPC, PE, PS, DPG, and phosphatidylinositol (PI) in the barley phospholipids. Linoleic acid was dominant in corn in the following fractions: PC, LPC, PI, PG, PE, DPG, and PA. Palmitic acid (16:0) was found at concentrations of 30% or more in the PS, PG, and PA fractions of both Kearney and Prilar and also in LPC of Kearney. However, in corn phospholipids only PI and PG were that high.

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Effects of Drying and Duration of Storage on the Extractable Atrazine Content of Soil Samples

The extractable atrazine content of soil samples was reduced by drying at 45 °C for 24 h. Dried samples originally containing 1 ppm atrazine showed no further significant loss of atrazine when stored up to 180 days at room temperature; however, there was significant loss between 180 and 360 days. Dried samples originally containing 10 ppm atrazine showed significant loss after 90 days of storage.

In experiments involving herbicide dissipation in the field it is often necessary to accumulate large numbers of soil samples over a growing season for chemical analysis of residual herbicide. If analytical results are to have any relevance to the field situation, dissipation of the herbicide during storage must be minimal, or at least predictable. Storage at temperatures of −15 to −20 °C is the preferred method, but when a large bulk of samples overtaxes available refrigerated storage, alternative storage procedures must be used. The experiment described in this paper was carried out to determine the effect of drying and subsequent storage at room temperature on the amount of extractable atrazine in soil samples.

MATERIALS AND METHODS

Birganbigil clay loam (van Dijk, 1961), containing 53% clay and 1.7% organic carbon, was fortified with atrazine to a concentration of 1 or 10 ppm. Atrazine was added as a solution of technical grade chemical in acetone. The solvent was allowed to evaporate before the soil was thoroughly mixed. Immediately after mixing, the control samples of each concentration were placed in screw-capped glass jars and stored at −20 °C. A second treatment of each concentration was placed in an oven at 45 °C for 24 h before being transferred to jars and stored in the same manner as the controls.

Water was added to the remaining samples to increase their moisture content from air-dry (8%) to a more typical field moisture (18%). They were then placed in brown paper bags and dried at 45 °C for 24 h, after which one set of samples of each concentration was transferred to glass jars and stored at −20 °C with the earlier samples. The remainder were stored at room temperature in the brown paper bags for 30, 90, 180, or 360 days. At the end of the allotted storage period, samples were transferred to jars and stored at −20 °C. Each sample contained 100 g of soil, and each treatment was replicated three times.

At the end of the experiment the samples were extracted by boiling in acetonitrile–water (9:1), and atrazine content was determined by the gas chromatographic method of Bowmer (1972). Cleanup of the dichloromethane solution was not necessary. Results were corrected for soil moisture content.

RESULTS AND DISCUSSION

Atrazine concentrations of the samples following the drying and storage treatments are given in Table I. The amount of atrazine extractable from the 1-ppm samples

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Table I. Effects of Drying Treatments and Duration of Storage on the Extractable Atrazine Content of Soil Samples

initial atrazine concn, ppm	prestorage treatment[a]	storage time, days	final atrazine concn, ppm
1	nil	nil	0.96 ± 0.076[b]
	heated	nil	0.94 ± 0.062
	moistened and heated	nil	0.85 ± 0.047
		30	0.81 ± 0.014
		90	0.86 ± 0.025
		180	0.87 ± 0.020
		360	0.59 ± 0.044
		SE	0.03
	LSD (P = 0.05)		0.09
10	nil	nil	8.35 ± 0.188
	heated	nil	7.96 ± 0.066
	moistened and heated	nil	7.62 ± 0.055
		30	7.49 ± 0.283
		90	7.23 ± 0.112
		180	6.79 ± 0.190
		360	5.04 ± 0.203
		SE	0.11
	LSD (P = 0.05)		0.33

[a] Heated to 45 °C for 24 h. Moisture content raised from 8 to 18% moisture prior to heating. [b] Standard deviation.

was not significantly decreased by heating the air-dry soil to 45 °C, but was decreased significantly if the soil was wetted before heating. Storage up to 180 days after drying produced no further reduction in atrazine recovery; however, there was a marked reduction between 180 and 360 days. After this longest storage time, only 61% of the atrazine was recovered.

When the 10-ppm sample frozen immediately after preparation was analyzed, only 8.35 ppm atrazine was recovered. It appears that either the atrazine was significantly degraded under frozen conditions, or that the herbicide was bound so strongly that the extraction system was unable to remove it completely from the soil.

When the 8.35-ppm concentration was taken as 100%, the percentage losses from the high concentration series showed a similar pattern to those of the 1-ppm series. As actual concentrations were higher, however, percentage errors due to the limitations of the extraction and determination procedures were lower, and more differences between treatments reached significance. Atrazine content was reduced on heating the soil sample, and loss was significantly greater if the soil was wetted before heating. Loss of atrazine during storage up to 180 days followed a first-order reaction with a half-life of 1082 days. Between 180 and 360 days, if a separate first-order reaction is assumed, the half-life decreased to 419 days. This increased dissipation rate during the second 180 days of storage may be a seasonal effect. The experiment was commenced in late autumn, and so the first half of the storage period included winter and spring, while the second half was in summer and autumn. Although storage was in a reasonably insulated interior room, it would be expected that temperature differences would occur in response to seasonal differences of at least 20 °C external daily maxima.

At both initial concentrations extractable atrazine was reduced by heating moistened soil to 45 °C for 24 h. This may have been due to atrazine hydrolysis during the period in which the soil was hot but still moist. Alternatively loss may have been by volatilization (Beestman and Deming, 1974), aided in the case of the moist soil by the "wick effect" (Hartley, 1976).

The disapperance of atrazine with time of storage agrees very closely with results obtained by Birk and Roadhouse (1964). They stored samples containing 1.5 or 7.5 ppm atrazine in glass jars at room temperature. After 55 days of storage, recovery was 96.8% of that at the commencement of the experiment. After 11 months, recovery of the 1.5-ppm samples had fallen to 58.1%, while that of the 7.5-ppm atrazine samples was 68.3% of the original recovery.

The results of this experiment indicate that caution should be exercised if it is necessary to store soil samples at room temperature prior to analysis for atrazine content. It appears that atrazine slowly dissipates or becomes tightly bound to soil components during storage, even at very low moisture contents. If this type of storage is necessary, spiked samples with herbicide contents and moisture contents similar to those of the unknown samples should undergo all drying and storage procedures, so that an accurate assessment of herbicide dissipation can be obtained. Storage should be in a room with a low, relatively constant temperature, and the period of storage should not exceed 6 months.

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