Dedicated
to

Renee, Kathy and My Family

ABSTRACT

M.Sc. Phillip C. Alexander Entomology

THE USE OF ATRAZINE IN CORN PRODUCTION

Post emergence sprays of 2½ pounds per acre of the herbicide atrazine were applied to eight acres of grain corn on tile-drained Ste. Rosalie clay soil near Ste. Anne de Bellevue in 1971 and 1972. Samples of soil, surface run-off water, sub-surface drainage water and of accumulations of drainage water in ponds were analysed at intervals from May to October. Residues in the soil varied from 0.001 to 0.139 parts per million: maximum residues in drainage water, in pond sediment and in surface run-off were 0.043, 0.043 and 0.0042 ppm. Spring carry-over residues were negligible.

An increase in detectable residues in soil and in run-off water was positively correlated with rainfall. Soil residues were in the 0-10 inch layer. Breakdown products were not investigated. Atrazine used in this way does not result in serious persistent residues in soil or soil water.

ABREGE

M.Sc. Phillip C. Alexander Entomologie

L'UTILISATION D'ATRAZINE DANS LA PRODUCTION DU MAÏS

Des arrosages (en pulvérisation) post-émergents, d'herbicide atrazine, à 2½ livres l'acre, furent appliqués à des semences de maïs, dans un Ste-Rosalie sol argileux à drainage tuilé, sur une étendue de 8 acres près de Ste-Anne de Bellevue. Des analyses systématiques furent exécutées sur des prélèvements du sol, des eaux de surface, des eaux profondes de drainage et des eaux amassées aux bassins de drainage. Les résidus du sol présentèrent une différence de 0.001 à 0.139 part au million; les résidus maxima des eaux de drainage, celles des bassins et des eaux de surface furent de 0.043, 0.043 et 0.0042 pts.m. respectivement. L'étude des eaux de printemps donna un produit de résidus négligeable.

Une augmentation appréciable de résidus du sol et des eaux de surface était directement attribuable à la tombée des pluies. Les résidus du sol furent prélevés au niveau de 0-10". Les produits secondaires ne furent pas examinés. Atrazine utilisé de la façon déjà mentionnée ne produit pas de quantité importante ou persistante de résidus dans le sol ou les eaux du sol.

THE USE OF ATRAZINE IN CORN PRODUCTION

by

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GLOSSARY

Common Name	Chemical Name
atrazine	2-Chloro-4-ethylamino-6-isopropylamino-s-triazine
captan	N (trichloromethylthio) 4-cyclohex-4-ene, 1,2, dicarboximide
diazinon	O,O,O, (2-isopropyl-6-methyl-4-pyrimidyl) phosphorothioate
Gardona (R)	2,-chloro-1-(2,4,5-trichlorophenyl) vinyl dimethylphosphate
lindane	gamma isomer 1,2,3,4,5,6, -hexachlorocyclo-hexane
malathion	Diethyl mercaptosuccinate-S-ester-O, O - dimethylphosphorodithioate
methoxychlor	1,1,1,-trichloro-2,2,-bis(p-methoxyphenyl) ethane
xVitaflo D.B.(R)	Tetramethyl thiuram disulphide (Thiram) 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide (Vitavax)

(R) = registered Trade Mark

x Vitaflo D.B. is a compound containing as its active ingredients, thiram and Vitavax

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INTRODUCTION

Atrazine, 2-chloro-4 ethylamino-6-isopropylamino-s-triazine is a chloro-substituted s-triazine herbicide and is widely used in agriculture as a pre- and post- emergence spray, and also as a soil sterilant for the chemical control of weeds and other broad-leaved plants. Because of its selective herbicidal activity and low phytotoxicity to corn, it has come to play a major role in the control of noxious weeds in the production of that crop.

In order that a sound weed control programme can be developed in any agricultural venture, it is always desirable to have a complete knowledge of the chemistry, behaviour, herbicidal activity and persistence of any herbicide or herbicides that are to be utilized. A knowledge of their behaviour eliminates the possibility of undue persistence of soil residues, which can then be effectively avoided by the selection and use of dosages which ensure proper weed control, but do not leave behind harmful residues.

While soil retention of a herbicidal residue may be advantageous in some cases for current weed control, it may on the other hand be detrimental to any herbicide-sensitive crop grown in succeeding years on the same acreage.

Atrazine has been the cause of serious concern due to its carry over effects on crops grown after corn, e.g., sugar beet (Frank, 1966).

Continuous application of atrazine on land on which corn is being grown season after season has resulted in no harmful effects to the corn. This is due to the ability of the corn plant to remove atrazine from the soil by root uptake, or leaf absorption, and break it down into non-phytotoxic metabolites (Shimabukuro _et al_., 1969).

OBJECT OF STUDY

The object of this study was to determine the fate of atrazine used as a herbicide in the production of corn.

An attempt has been made to determine persistence in, and the rate of disappearance of this compound from the soil, run-off water, and lake bottom sediment under practical field conditions.

REVIEW OF LITERATURE

The literature available on atrazine and other triazine herbicides is very extensive. Several reviews of the literature have appeared in recent years, e.g., those of Gysin and Knuesli (1960), Knuesli (1970), and Frear et al. (1972).

Some of the most pertinent papers in the literature are briefly reviewed here.

PERSISTENCE

The persistence of any pesticide in the environment can be determined or assessed by its continued activity. Birk and Roadhouse (1964) showed that 90% of residual atrazine was in the 0-2" depth of soil one to two years after application at rates ranging from 2 to 20 lb/acre. Most of the 90% was in the 0-1" layer. The same authors compared persistence of atrazine in corn plots to that in fallow soil. At the end of the first season, residues were much greater in the soil that had been cropped than in the fallow soil.

Talbert et al. (1965) showed that 0.16 lb/acre of atrazine was present one year after a soil application of 2 lb/acre. Buchholtz (1965) reported greater persistence of atrazine during dry summers than during summers with abundant rainfall. In addition soil samples taken 1, 2, 3 and 6 months after application show that variables other than date of application influence the relative carry-over rate of any triazine applied to soil. Such samples from plots of corn and Johnson grass sprayed with 2,4, and 15 lb/acre contained smaller residues of atrazine in the 0-6" depth than samples from fallow plots sprayed at the same rate.

Harris et al. (1969) surveyed the persistence of atrazine placed 3, 9 and 15" deep under sod in twelve geographically separated soils throughout the United States and Puerto Rico. In general persistence increased with depth, lower temperature, and higher organic matter content with an average of 51% more atrazine recovered from sub-surface soils at the 15" level than from surface soils at the 3" level after treatment with equal amounts of atrazine under field conditions. On the other hand, residue carry-over from atrazine was found by Burnside et al. (1969) to be concentrated in the top six inches of six soils studied. However, significant leaching did occur in a very fine sandy loam soil with unusually heavy rainfall.

Wolcott (1970) has indicated that disappearance of a measureable or recognized activity provides no assurance that the chemical has been removed or altered in its essential chemistry.

Sheets (1970) contends that the soil environment in which an herbicide is introduced determines its rate of disappearance. Hence, differences in persistence among soils may be determined by variations of temperature and moisture levels.

The same author, however, is of the opinion that because of the fact that run-off removes most of any material or reduces a herbicidal residue, does not necessarily mean that the herbicide molecule ceases to exist in other parts of the environment.

ADSORPTION

Recent attention has been focussed on the adsorption of pesticides on various substrates in the soil environment.

Harris and Warren (1964) have indicated that the limited solubility of atrazine enhances its adsorption by soil components particularly the organic fraction. Harris et al. (1964) and Talbert et al. (1965) found that adsorption was not related to the water solubility of the compound.

Bailey and White (1964), on the other hand, from their observations conclude that the relationship existing between solubility and the extent of adsorption appears to be valid only within a family of compounds.

Harris *et al*. (1964) and Talbert *et al*. (1965) reported that the adsorption of atrazine increased with decreased temperature and that the availability of atrazine was greater at a higher temperature. Harris and Warren (1964) and Talbert and Fletchall (1965) investigated the effect of pH on atrazine adsorption. They concluded that adsorption of atrazine varies inversely with pH.

McGlamery *et al*. (1966) found that atrazine adsorption onto soil and humic acid isolated from leonardite increased as pH decreased, but adsorption was only slightly affected by the parameters, temperature, and concentration of the adsorbate.

McGlamery and Slife (1966) studied the adsorption from an aqueous solution of atrazine on a Drummer silty clay loam and on humic acid. Adsorption on the soil was greater at pH 3.9 than at 8.0, and at 0°C than at 40°C.

Nearpass (1967), while studying the effect of the predominating cation on the adsorption of atrazine in soils, found that the adsorption of atrazine is governed largely by the hydrogen ion activity relationship which occurred between the solution and the solid phase of the soil.

Nearpass (1967) found that adsorption from aqueous solutions of atrazine by a Bayboro clay soil was dependent upon the exchange acidity of the soil. Armstrong et al. (1967) showed that hydrolysis of atrazine to hydroxyatrazine is catalyzed by adsorption onto organic matter with hydroxyatrazine more strongly adsorbed than atrazine.

Weber et al. (1968), however, contend that any treatment which decreases soil pH tends to reduce triazine phytotoxicity. This was controlled by greater protonation of the triazine at lower pH resulting in increased soil adsorption.

Harris et al. (1969) have suggested that increasing adsorption with a decreased temperature may be a factor in movement and activity of pesticides in soils and in increasing persistence with increasing depth.

Weber (1970) pointed out that triazines are readily adsorbed by a variety of clay minerals. This adsorption is dependent upon acidity of the aqueous systems and tend to increase with a decrease in pH.

MOVEMENT

Movement studies of atrazine and other soil applied herbicides have been documented by several research workers.

Hartley (1961) indicated that several years would be necessary for as little as 1% of the concentration of surface applied herbicides to migrate by diffusion to a depth of two feet in a moist soil.

White et al. (1967) found that low levels of atrazine were carried off by surface water moving off sprayed fields during and after application. He used simulated rainfall. Most of the atrazine was retained in the upper 3" of the soil profile. No measureable quantities were found below 6". Terracing was not used to hinder run-off water from leaving the field.

White et al. (1967) are of the opinion that the temperature at the time of the rainfall would also contribute to differences in atrazine content in run-off water. "Run-off" water is defined as water as it immediately leaves a specific field. Bailey et al. (1970) have suggested four principal means of pesticide transport within soils - (1) diffusion in air spaces of soil; (2) diffusion in soil water; (3) transportation by downward flowing water; and (4) transportation by water moving upward.

Bailey et al. (1970) contend that percolating water is the principal means of movement of the relatively non-volatile pesticides and diffusion of soil water is important only for transport over very small distances.

The same authors reported that the total amount of rainfall and frequency of received water all appear to affect the movement of herbicides in the soil. This movement is dependent on soil type with a greater amount of leaching of a pesticide in the soil profile occurring with a greater amount and frequency of rainfall.

Sheets (1970) indicates that weather and climate influence the disappearance of herbicides through the effect of their surface removal in run-off water, and downward movement in the soil profile.

Bailey and White (1970) have reported that movement of atrazine is at an optimum in light textured soils.

MOBILITY

Triazine herbicides are considered to be rather immobile in the soil. Roadhouse and Birk (1964) and Bauman and Williams (1966) tend to believe that atrazine is immobile in the soil. Helling (1970) contends that such a generalization must be tempered by recognizing that due to the fact that leaching is greater in sandy soil than in other soils, mobility differences do exist among individual triazines. Helling et al. (1971) have indicated that the mobility of s-triazine herbicides in soils is influenced both by soil and pesticide factors.

LEACHING

Herbicides when applied pre- or post-emergence are subject to severe leaching. Leaching tends to affect herbicidal activity by the removal of the herbicide from its active site with its subsequent transportation to a region where it is relatively non-functional.

Upchurch and Pierce (1957 and 1958) have indicated that at least two steps are involved in the leachability of a herbicide - (1) entrance of the compound into solution, and (2) adsorption of the compound onto the soil particles. Entrance of the pesticide into solution can take place either from the dissolution of the pesticide present in particulate form or from the pesticide present on colloidal surfaces. Several investigators have attempted to determine the amount of leaching which atrazine undergoes when applied as a herbicide.

Montgomery and Freed (1959) found that the maximum concentration of C^{14} atrazine to be at 7-8" after leaching a Chehalis sandy loam column with 12" of water during three days.

Burnside et al. (1963) showed that in Rosebud loam plots higher concentrations of atrazine were found below 12" than in the upper 6", 16 months after application. Hartley (1964) is of the opinion that the leaching of a herbicide into soil is influenced by the moisture level of the soil at the time of application and by evaporation rate.

Harris (1966) showed that pesticides are leached to a greater degree in light textured soils than in heavier textured soils. Bauman and Williams (1966) reported that within six months after field application of atrazine in Indiana, the herbicide had leached to 2-4", though most remained at 0-2".

LeBaron (1970) investigated by means of soil residue analysis, a number of soils which had been treated annually with triazine herbicides for several years. He found that levels of residues below the 8-12" depth seldom showed any significance except in light textured soils with little organic matter and with high rates of triazine application which occasionally resulted in some accumulation at lower depths.

USE OF WATER

Water appears to play an important role in influencing herbicidal activity. Hance et al. (1965) have indicated that varying moisture content is a real factor in the behaviour of herbicides in the field. Lambert et al. (1965) have reported that soil moisture content influences the concentration of pesticides in the soil solution, a factor of considerable importance in the expression of herbicidal activity.

Roeth et al. (1969) found that by increasing the moisture content from 40% to 80% of field capacity, six times as much metabolism of atrazine was obtained. Atrazine was degraded two to three times faster in top soil compared to sub-soil. LeBaron (1970) suggested that water can be useful in reducing or eliminating soil carry-over of triazines.

Switzer and Kauser (1970) found that 2 lb/acre of atrazine was detoxified in eight weeks under conditions of high moisture content and temperature, while under dry conditions the same rate caused oat injury twelve months later.

TEMPERATURE

The role of temperature in the regulation of triazine activity in soils cannot be overemphasized.

Kearney et al. (1964) suggested that field atrazine losses may be significant under high soil temperature conditions. Bailey and White (1964) have indicated that the solubility of herbicides and adsorption by soil particles would both be influenced by temperature. McCormick and Hiltbold (1966), Roeth and Lavy (1969) reported that the degradation rate of atrazine increased two to three fold for each 10°C temperature increase from 15° to 35°C.

DEGRADATION

Most pesticides break down quite rapidly in our environment. The soil usually provides the site for their conversion to small fragments. Pesticides are reactive and their degradation may be of a significance in determining and controlling their persistence in the environment, and hence reducing their undesirable effects.

Degradative processes can occur either through biological or non-biological pathways. The rate of retention of any pesticide in a soil or other surroundings can be influenced by the several factors which affect their degradation.

NON-BIOLOGICAL DEGRADATION

Horrobin (1963) showed that hydrolysis of chloro-s-triazines occurred stepwise with replacement of one chlorine atom with hydrolysis speeding up with increased alkalinity or acidity.

McCormick and Hiltbold (1966) found that atrazine hydrolysis followed a first order kinetics reaction in sterilized soil and in perfusion systems. Hydrolysis of atrazine occurred after 10 days in aqueous solution at pH 2 and 12, 100 days at pH 4 and 11.

These two authors found that soil pH and organic matter largely control the rate of atrazine hydroxylation and that hydrolysis occurs in strongly basic or acidic solutions.

Harris (1967) examined the effect of temperature on the loss of atrazine in four soils. He identified the hydroxy derivative in methanol extracts of soil as a degradation product. Increasing soil temperature from 30°C to 95°C greatly increased the conversion of atrazine to hydroxyatrazine, whereas increasing the temperature of an aqueous solution of atrazine without soil had only a slight effect.

Skipper (1967) suggested that atrazine degradation is a direct chemical hydrolysis rather than a result of microbial attack. Microbial attack possibly occurs on the side chain with a low rate of attack on the atrazine ring upon hydrolysis to hydroxyatrazine with degradation decreasing with time. Hance (1967) measured the non-biological decomposition of atrazine and five other herbicides in aqueous solutions in two soils in a bentonite clay suspension. He found that the half life of atrazine was related to temperature. It ranged in the bentonite suspension from 180 hours at 107°C to 116 years at 20°C. His conclusion was that non-biological processes do not play an important part in the loss of atrazine from the soil and that hydrolysis of the s-triazines is pH dependent.

Harris (1967) studied triazine degradation in soils and found that approximately 30 to 50% of the chloro-s-triazine was converted to the hydroxy compound in 8 weeks at 30°C. This suggested that soil constituents catalyzed a non-biological hydrolysis reaction. Armstrong and Chesters (1968) seem to support the above author's view. Harris (1967) showed that the presence in soil of 200 ppm of sodium azide, a microbial inhibitor, had little effect on the accumulation of hydroxy derivatives of atrazine, thus suggesting a mechanism other than microbial degradation. Weber (1970) suggested that because of its pH dependence, non-biological hydrolysis of s-triazines is probably an important process in relatively acid soils. Helling et al. (1971) believe that in reality chloro-s-triazines are primarily degraded by purely chemical means.

BIOLOGICAL DEGRADATION

Kaufman and Kearney (1970) indicated that microbial degradation of chloro-s-triazine herbicide occurs by the N-dealkylation route. Skipper and Volk (1972) reported that increased temperature, moisture and organic matter content of soils stimulate microbial degradation of s-triazine herbicides in soil.

PLANT METABOLISM AND UPTAKE

In considering the various factors involved in the removal and dissipation of triazine herbicides from the soil, the role of the plant should not go unnoticed.

Gysin and Knuesli (1960) reported that chloro-s-triazines can be metabolized readily by corn.

Sikka and Davis (1966) reported that corn as well as sorghum were effective in reducing the amount of atrazine remaining in the soil in both field and greenhouse studies. Recent work seems to suggest that atrazine is metabolized by corn and transformed into non-phytotoxic water soluble metabolites (Shimabukuro _et al_., 1966).

Shimabukuro (1967) indicated that the rate and pathways of atrazine metabolism are important in determining the tolerance of plants to the herbicide. The primary factor which seems to determine the tolerance of plants to triazine herbicides is the ability to degrade and detoxify the phytotoxic parent molecule.

Shimabukuro (1968) found that atrazine was metabolized by corn to non-phytotoxic hydroxylated compounds and N-dealkylated metabolites. This ability of corn to convert triazine to a non-phytotoxic compound is the basis of its herbicidal selectivity. The conversion of the 2-chloro-s-triazines is catalyzed non enzymatically by the presence of benzoxazinone in the corn plant.

Roeth and Lavy (1969) found that the ability of corn roots and shoots to quickly degrade atrazine to hydroxy atrazine was undoubtedly very important in the tolerance of corn to atrazine. Le Baron (1970) however contends that several investigators have failed to find any significant advantage in a crop of corn to enhance atrazine dissipation.

Frear and Swanson (1970) have shown that atrazine metabolism in corn is dependent on the activity of an enzyme glutathione-s-transferase.

Shimabukuro _et al_. (1971) have shown that the primary factor for atrazine selectivity in corn is the activity of the soluble enzyme glutathione-s-transferase which detoxifies atrazine by catalyzing the formation of an atrazine-glutathione conjugate. While the non-enzymatic compound benzoxazinone catalyzed the hydrolysis of atrazine to hydroxy-atrazine, the non-enzymatic detoxication pathway did not seem to be essential for resistance.

MATERIALS AND METHODS

Atrazine recovery studies were undertaken on an area of land of approximately eight acres situated near the upper lake (see map in Appendix) on the Macdonald College Farm. This plot of land was tile drained. The soil type was a Ste. Rosalie clay loam. Field run-off water from the plot fed into two tile drains, TD4 and TD5, respectively. Surface run-off water emptied into a weir adjacent to the most northerly part of the field. Field run-off, tile drain and weir water all finally emptied into the upper lake. The field plot was subjected to standard agricultural practices, viz. ploughing, disc harrowing and the annual application of a herbicide for weed control. Field application of fertilizer occurred just before planting time in early spring.

The corn varieties used in this experiment were U.H.106, U.H.108 and Pride 5. All seeds were pretreated as follows with (1) Diazinon 15%-Lindane (BHC) 25%, applied at a dosage rate of 2 oz. per bushel, (2) methoxychlor 0.37 oz. per bushel and (3) Vitaflo D.B.$^{(R)*}$, a fungicide, at a rate of 2 oz. per bushel. The seeds had been pretreated by the seed company with captan, thiram and malathion at an unspecified dosage

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*See Glossary

rate. The rate, mode and time of application of Gardona (R)* and atrazine to the experimental plot No. 5 are summarized in Table 1. This plot of land was seeded on the 30th May 1971.

Table 1. Field Treatments 1971-1972

Pesticide	Formulation	Dosage per Acre	Mode of Application
Atrazine	80W	2½ lb actual -	Post-emergence spray
Gardona (R)	75W	¾ lb per acre -	Sprayed on 8 weeks after planting

The chemical name and structural formula of atrazine is given in Figure 1.

Solvents used for soil, water and sediment analyses were all Toxigraphic** grade reagents and were obtained from Anachemia Chemicals Ltd., Canada.

2-chloro-4-ethylamino-6-isopropylamino-s-triazine

ATRAZINE

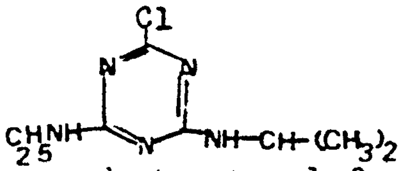

Figure 1. Chemical name and structural formula of atrazine.

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* See Glossary. Gardona was applied 3 weeks after planting time in 1971 and 1972.

** A Toxigraphic grade reagent is defined as a reagent which has been glass distilled, specially purified and containing only one half part per million residue and no interfering substances greater than 10 parts per billion.

The analysis and quantification of soil, water and sediment residues were accomplished using a Varian 1400 gas chromatograph equipped with an alkali flame ionization detector, sensitive to phosphorus and nitrogen-containing compounds. A spirally coiled brass column 5 feet long and 1/8 inch diameter was used. The solid phase was 1% OV-1 on Porapack 30 (100/120 mesh).

SOIL SAMPLING

In the first year (1971), soil sampling was undertaken from eight sampling sites and at two soil depths, (0-10") and (10-20"). Two grid lines (see map in Appendix) 300 feet long and 300 feet apart were used as location guides for the soil sampling sites in the field. Four points, A, B, C and D along each grid line were used as the soil sampling sites. A was 40 feet from the field edge, B was 60 feet from A, C was 80 feet from B, and D was 150 feet from C. Individual sampling sites were called either IA or IIC, etc. depending on the particular grid line to which they belonged. Soil sampling was undertaken by the use of a soil auger. Storage was in a refrigerator at -20°C. Soil was stored in 400 g Mason jars. Sampling was undertaken as follows: The first day, after herbicidal application, a week after, two weeks after and subsequently every month until October 1971. In the following year (1972) sampling sites were selected slightly differently. Five sampling sites were chosen on each of two grid lines A and B, respectively. These areas were designated as A1 or B2 dependent on which of the two grid lines that they were located. Samples were taken at 0-10" depth one day after herbicidal application, 3 days after, 1 week after, 2 weeks after, 3 weeks after and subsequently every month until September 1972.

WATER SAMPLING

Water samples were taken at the same sampling intervals as the soil samples. Sampling sites for water collection were the two tile drains, TD4 and TD5, respectively, an adjacent weir; upper and lower portions of the upper lake on the Macdonald College Farm. Water was stored in 2-litre flasks at 20°C in a cold room.

SEDIMENT SAMPLING

No special attention was paid to either lake bottom or tile drain sediment in the first year (1971). Samples were taken from the two tile drains TD4 and TD5, and from other areas situated in the upper and lower portions of the upper lake (see map in Appendix). Sediment samples were stored in a refrigerator at -20°C in 400 g Mason glass jars.

ANALYTICAL PROCEDURES

SOIL EXTRACTION

Soil extraction of atrazine has been reported by various workers, Roadhouse and Birk (1961), McGlamery et al. (1967), Mattson et al. (1970). For the atrazine recovery study, the method of Mattson et al. (1970) was adopted with slight modifications. Two solvent systems were used. In the first year (1971), an acetonitrile-water mixture (90:10) was used. The following year (1972), a methanol-water mixture (90:10) was used because it gave better recovery values.

Two hundred millilitres of a methanol-water mixture (90:10) was added to 100 g of air-dried soil in a Waring blender jar. The mixture was blended for 5 minutes and allowed to stand overnight. This was subsequently reblended the following day, filtered, the supernatant liquid transferred to a 500 ml flask and then evaporator. The solution remaining in the flask was then transferred to a 500 ml separatory funnel. This was diluted by the addition of 300 ml of water, then 25 ml of saturated sodium sulphate solution.

Extraction of this reaction mixture was carried out by using two 25 ml portions of methylene dichloride. The aqueous layer of this reaction mixture was discarded. The solvent layer was dried with sodium sulphate and evaporated to about 5 ml and allowed to stand for subsequent column clean up. (See under sedimentand soil samples).

WATER EXTRACTION

The methods of Abbot et al. (1965) and Tindle et al. (1968) were used with modifications for water extraction. Three hundred millilitres of water were placed in a 500 ml separatory funnel. To this was added two 50 ml portions of a 30% diethyl ether methylene dichloride solution. This was allowed to stand for about two hours altogether. The aqueous layer after extraction was discarded. The solvent layer was dried with sodium sulphate and then evaporated to about 5 ml on a Buchler flask evaporator. The eluate was then transferred to a test tube (130 x 10 mm) by means of a fine pipette using 5 ml of acetone in small portions and stored in a refrigerator for analysis by gas liquid chromatography.

SEDIMENT EXTRACTION

The method used for the extraction of sediment samples was similar to that used for soil analysis, save for a few modifications.

One hundred grams of air-dried sediment material was placed in a blending jar. To this was added 50 ml of methylene dichloride. This was allowed to stand for two hours. The solvent layer was removed and a further 50 ml of methylene dichloride were added to the jar. The two solvent layers were then combined, dried with sodium sulphate and evaporated to about 5 ml using a Buchler flash evaporator and then stored for subsequent column clean up.

COLUMN CLEAN UP

Water Samples

Analysis of water samples by column clean up was found to be unnecessary. Abbot et al. (1965) and Tindle et al. (1968) found that the amount of coextractives in water was negligible. The values for samples subjected to column clean-up were found to be not significantly different, hence the lack of need for clean-up of the water samples.

Sediment and Soil Samples

Similar procedures were followed for column clean-up of soil and sediment samples. Woelm basic alumina Activity Grade V, viz. 81% Aluminium oxide-19% water were used as the solid support. A glass wool plug was placed at the bottom of the glass column. A Pyrex tube (20 mm ID x 30 cm) fitted with a glass joint (24/40). Twelve and a half grams of Woelm at the top and a Teflon stop cork (2 mm bore) at the elution end was used to support the column, alumina were then added. The column was tapped gently to settle the packing and a glass wool plug was placed on top of the alumina. The sample was transferred quantitatively to the column using two 5 ml portions of carbon tetrachloride. When the last five ml portion had just penetrated into the alumina, a further 50 ml of carbon tetrachloride was added to the clean-up column. The eluate was discarded when the carbon tetrachloride just disappeared into the glass wool, 50 ml of a 5% diethyl ether in methylene-dichloride was added to the column. The eluate was collected in a 1,000 ml distillation flask, then evaporated using a Buchler flash evaporator and then transferred to a test tube by means of a fine pipette using 5 ml of acetone in small portions and allowed to stand for analysis by gas liquid chromatography.

GAS LIQUID CHROMATOGRAPHY

The carrier gas used in the Varian 1400 gas chromatograph was nitrogen. The flow rate of this gas was 30 ml/minute ± 5 ml. The flow of hydrogen and air was adjusted each day with needle valves on the instrument to give maximum sensitivity. The column temperature was 200°C, injection port temperature 225°C, with detection temperature at 250°C. Before injection, samples which were allowed to stand after column clean-up were carefully evaporated just to dryness using nitrogen. Samples were subsequently diluted by adding 0.1 ml of acetone. One micro-litre of each sample was injected into the gas chromatograph using a Hamilton microsyringe. Duplicate injections of each sample were made. A Honeywell strip chart recorder was attached to the gas chromatograph.

Individual peaks were identified by reference to quantitative standards supplied by Ciba-Geigy Canada Ltd. Unknown samples were subjected to gas liquid phase chromatography under the same operating conditions as the reference standards. Peak areas were determined by the peak height method. In order to maintain constancy in the operating conditions for sample analyses, standards were run on an hourly basis along with unknown samples. Soil residues in parts per million were calculated using the equation based on work described in the Canadian Food and Drug Directorate Pesticide Analytical Manual 1969.

$$\text{ppm} = \frac{\text{sample peak height}}{\text{std. peak height}} \times \frac{\text{vol. of sample}}{\text{injection vol.}} \times \frac{\text{ng of std./injection}}{\text{weight of sample}}$$

$$= \frac{\text{cm}}{\text{cm}} \times \frac{\text{ml of sample}}{\text{ul of sample}} \times \frac{\text{ng standard/injection}}{\text{g}} = \frac{\text{ug}}{\text{g}}$$

(MCLEOD ET AL 1969)

RESULTS

The data presented here represent values obtained for soil samples for the two years 1971 and 1972, respectively.

SOIL RESIDUES

Mean values for different sampling dates are presented in Tables 2 and 3 for 16 and 10 locations in 1971 and 1972, respectively.

Day one, 1971 was the day on which soil samples were taken before application of the herbicide (Table 6). Day 13 was the day on which the soil was treated that year. Day zero in 1972 was the day the soil samples were taken before application of the herbicide (Table 6). Day 1 was the first sampling date following soil treatment (Table 3).

The highest concentration of atrazine was obtained in the 0-10" soil layer, seven days after application in the first year, and three days after application in the second year (Tables 2 and 3). Twice as much atrazine was present the day after treatment in the 0-10" soil samples in 1972 as was present in corresponding samples in 1971 (Tables 3 and 2). The highest value obtained for atrazine in the 10-20" soil layer was on day 21 in the first year (Table 2). No values

Table 2. Atrazine (parts/million) in the soil of Field No. 5 Macdonald College Farm 1971. Atrazine in the soil of Field No. 5 at different locations.

Day No.	Sampling Date	Sample Depth	Locations IA	IB	IC	ID	2A	2B	2C	2D	Mean
14	10/6/71	0-10"	0.098	0.078	0.059	0.103	0.030	0.097	0.293	0.080	0.105
		10-20"	<0.001	<0.001	<0.001	0.043	<0.001	<0.001	<0.001	<0.001	0.005
21	17/6/71	0-10"	0.029	0.400	0.230	0.330	0.070	0.061	0.070	0.038	0.154
		10-20"	0.096	0.049	0.025	0.109	0.027	0.014	0.119	0.017	0.057
36	2/7/71	0-10"	0.010	0.080	0.022	0.042	0.378	0.010	0.011	0.002	0.069
		10-20"	0.026	0.010	0.008	0.004	0.135	0.002	0.002	0.001	0.024
61	27/7/71	0-10"	0.003	0.002	0.004	0.006	0.004	0.006	0.004	0.004	0.004
		10-20	0.004	<0.001	0.004	0.002	0.001	0.002	0.001	0.002	0.003
69	4/8/71	0-10"	0.002	0.049	0.003	0.003	0.002	0.003	0.001	0.042	0.014
		10-20"	0.006	0.014	0.035	0.004	N.S.	0.004	0.002	0.008	0.012
80	15/8/71	0-10"	0.003	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.002
		10-20"	0.002	N.S.	0.002	0.005	0.012	0.005	0.003	0.012	0.006
96	31/8/71	0-10"	0.001	0.001	0.001	0.003	0.002	0.003	0.002	0.002	0.002
		10-20"	<0.001	<0.001	0.008	0.001	<0.001	0.001	0.002	<0.001	0.002
116	20/9/71	0-10"	0.008	0.008	0.004	0.010	0.009	0.010	0.006	0.006	0.009
		10-20"	<0.001	0.002	0.003	0.003	0.003	0.003	0.005	0.007	0.003
146	20/10/71	0-10"	0.027	0.004	0.003	0.004	N.S.	0.004	0.002	0.008	0.007
		10-20"	0.002	0.002	<0.001	0.001	<0.001	0.001	<0.001	0.002	0.001

N.S. = Not sampled.

<0.001 (parts/million) = an amount less than the detection limit of 0.001 ppm.

Table 3. Atrazine (parts/million) in the soil of Field No. 5 Macdonald College Farm 1972. Atrazine in the soil of Field No. 5 at different locations.

Day No.	Sampling Date	Sample Depth	Locations A1	A2	A3	A4	A5	B1	B2	B3	B4	B5	Mean
1*	24/5/72	0-10"	0.938	0.212	0.397	0.186	0.274	0.205	0.014	0.085	0.389	0.285	0.298
3	26/5/72	0-10"	1.045	1.139	0.201	0.354	0.900	0.562	0.062	0.321	0.446	0.113	0.514
7	30/5/72	0-10"	0.249	0.027	0.049	0.069	0.041	0.222	0.004	0.278	0.057	0.243	0.124
14	6/6/72	0-10"	0.063	0.027	0.040	0.039	0.112	0.108	0.077	0.023	0.012	0.015	0.051
21	13/6/72	0-10"	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	
28	20/6/72	0-10"	0.141	0.082	0.406	0.052	0.021	0.119	0.145	0.059	0.118	0.094	0.124
58	20/7/72	0-10"	0.135	0.174	0.134	0.044	0.009	0.110	0.021	0.177	0.077	0.031	0.091
93	24/8/72	0-10"	0.013	0.010	0.011	0.009	0.035	0.013	0.015	0.007	0.033	0.115	0.025
128	28/9/72	0-10"	0.031	0.016	0.047	0.020	0.007	0.008	0.016	<0.001	0.058	0.076	0.028

N.S. = Not sampled.

*One day after herbicidal application.

were obtained on day 21 in the second year (Table 3). This was a result of a severe thunder and rainstorm which prevented completion of the sampling. The residue data in the 0-10" soil layer for both years for the last sampling dates show four times as much atrazine present in 1972 as was present in 1971. There was a greater penetration of atrazine into the 0-10" soil layer during the early part of the second year than in the corresponding period of the first year (Tables 3 and 2). Concentration of residues in parts per million plotted against sampling dates in the first year for the 0-10" and 10-20" soil layers are presented in Figure 2.

The curves for residues in the 10-20" soil layer follow a pattern similar to that obtained for residues in the 0-10" soil layer (Figure 2). The highest residues for 1972 appear on day 3 (Figure 3). The residue pattern in the second year was similar to that for 1971 (Figures 2 and 3).

The total amounts of residues were determined for each month during the sampling periods. These values were arrived at by totalling the means of residue values obtained for each of the 10 or 16 locations for each sampling date for each month and expressing them as monthly totals versus total residues for the year. The frequency distribution of soil residues in parts per million versus monthly totals for the two years are indicated in Figure 4. The histogram shows

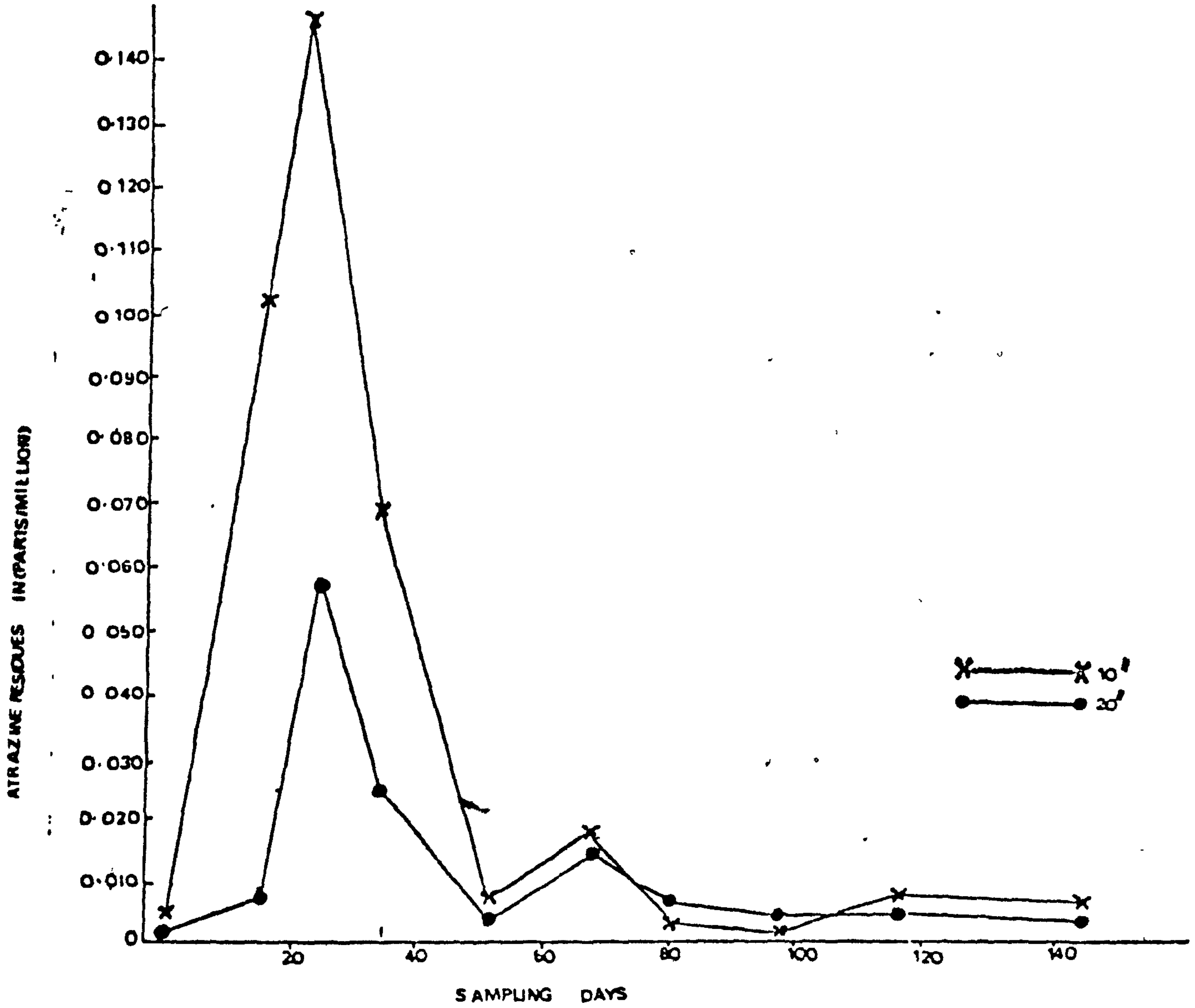

Figure 2. Soil residues (atrazine) Macdonald College Farm 1971.

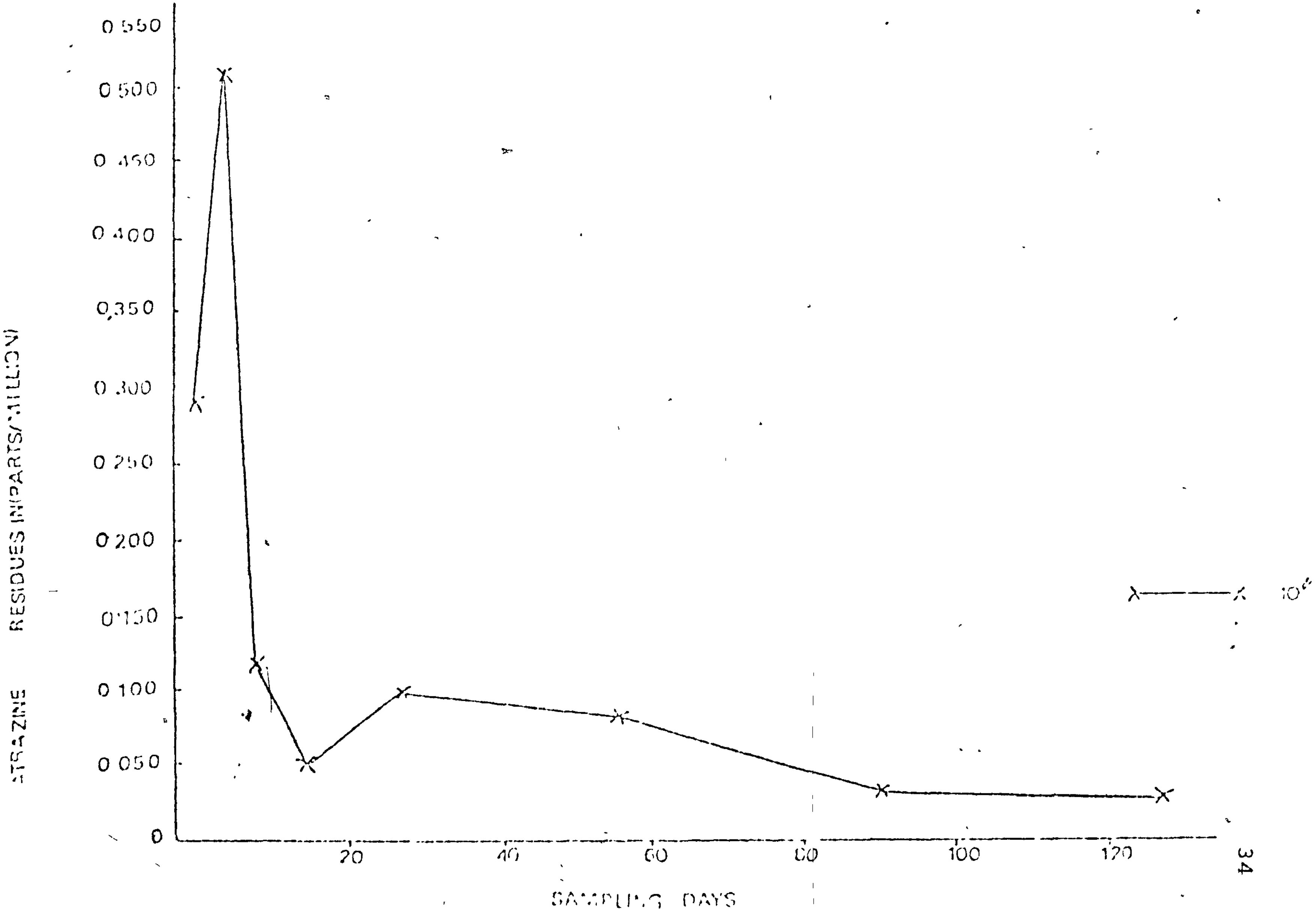

Figure 3. Soil residues (atrazine) Macdonald College Farm 1972.

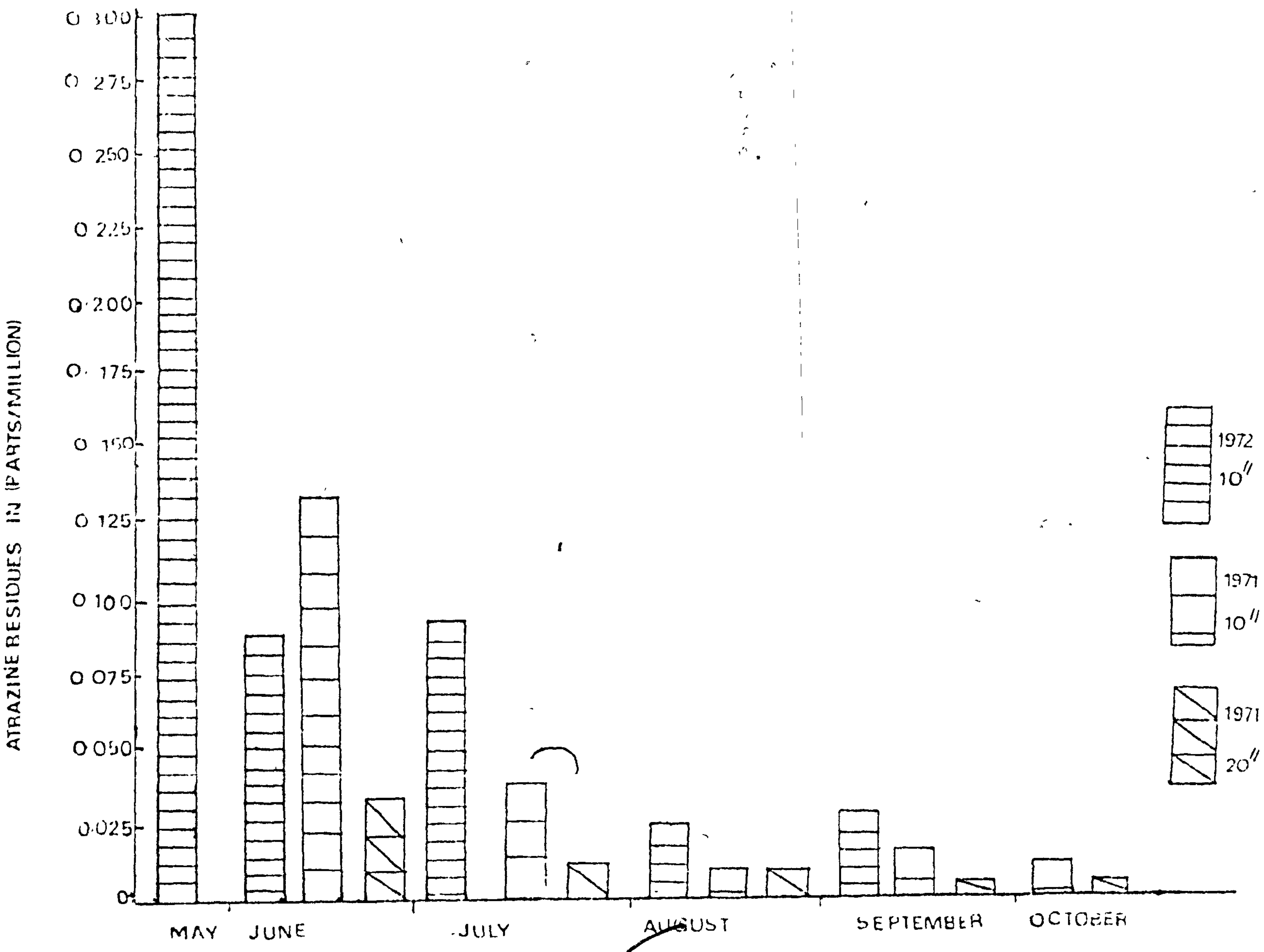

Figure 4. Frequency distribution of atrazine residues in soil 1971-1972.

that the highest residual concentration of atrazine occurred in the early part of 1972 in the 0-10" soil layer. The amounts of atrazine decreased progressively from May until August, then the levels remained relatively constant from August until the end of the sampling time. Residue decrease in 1972 in the 0-10" soil layer followed the same trend that was observed in 1971 (Figure 4). There was a high value in May followed by a decrease in values until August. In the 10-20" soil layer in 1971 most atrazine was found in the month of May.

All residues tended to be much higher on certain sampling dates than on others (Figures 2, 3 and 4). Measurement of actual rainfall on sampling days (Table 4) indicates little relationship with total amounts of residue. However, when monthly rainfall (Figure 5) is compared with average residue found in each month, it appears that rainfall is correlated with high detectable residues.

The level of residues present on the experimental plot before application of atrazine in 1971 was determined by analysis of soil samples taken prior to soil treatment. This procedure was repeated in the second year. The object was to determine if climatic factors influenced accumulation of residues at different soil depths. The data obtained for the soil sample analyses prior to treatment in successive years

Table 4. Rainfall on sampling days 1971-1972.

Day No.	Sampling Date	Rainfall In Inches On Same Date	Day No.	Sampling Date	Rainfall In Inches On Same Date
1	27/5/71	0.20	1	8/5/72	0.10
14	10/6/71	0.04	14	6/6/72	0.29
21	17/6/71	0.20	21	13/6/72	0.08
36	2/7/71	0.02	28	20/6/72	0.30
61	27/7/71	0.31	58	20/7/72	0.70
69	4/8/71	0.03	93	29/8/72	0.30
80	15/8/71	0.25	128	28/9/72	0.14
96	31/8/71	0.06			
116	20/9/71	0.29			
146	20/10/71	0.01			

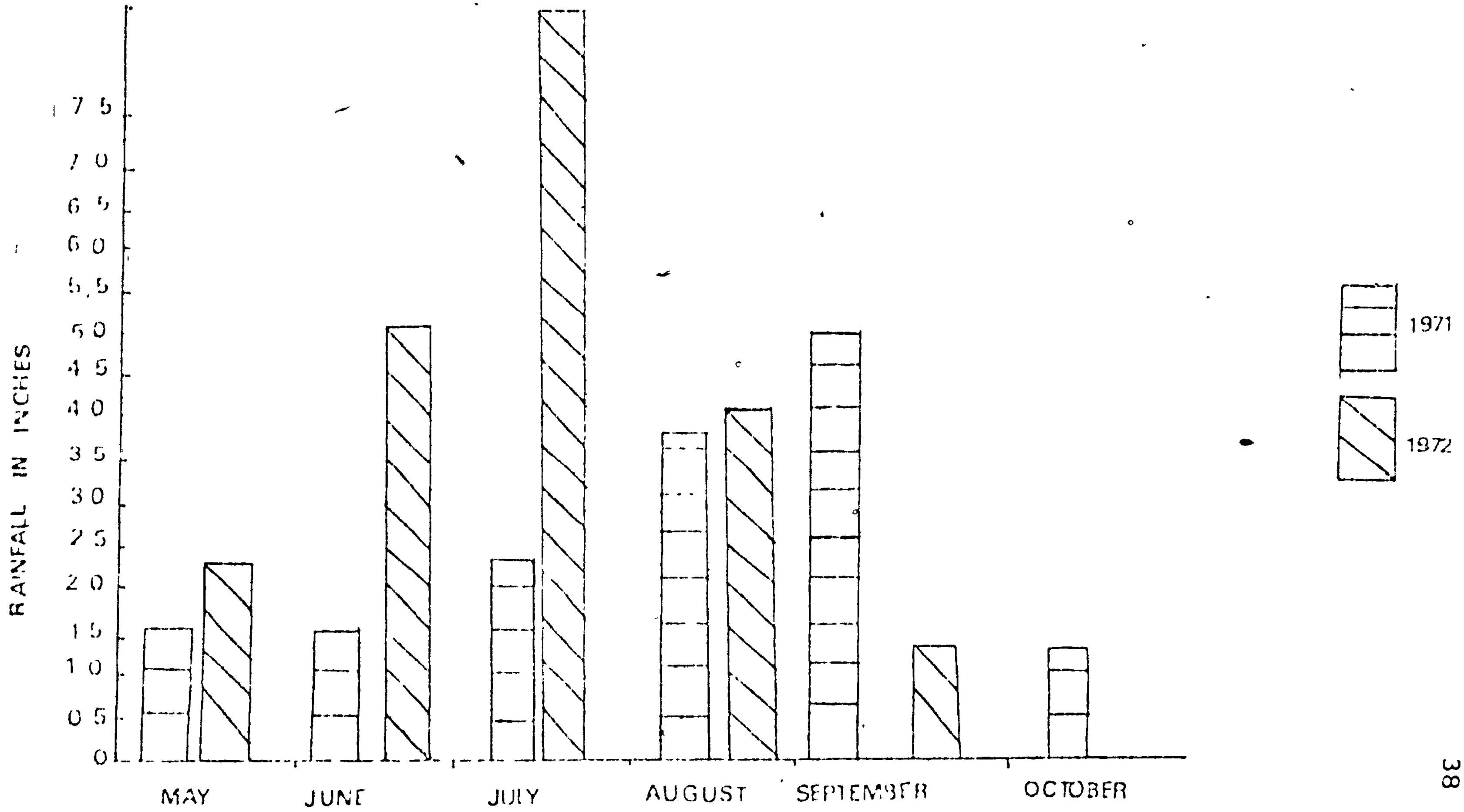

Figure 5. Monthly rainfall 1971-1972.

are presented in Table 6. The residue levels prior to treatment were not significantly different in the two years. Accumulation of residues in the 0-10" and 10-20" soil layers in the first year was well below the detection limit for soil samples analyzed during the course of this study.

Limit of Detection

Each gas chromatograph has its limit of sensitivity to each compound being detected. For the purposes of this study, the instrument used was an alkali flame ionization detector. The minimum detectable peak was taken as three times the noise level. Noise level can be best defined as the variation in the baseline of a chromatogram drawn by a recorder pen relative to the peak height value obtained for a particular sample. This was found to be 1mm. For a concentration of 0.5 ng of atrazine, a peak height of 3mm was obtained, and this was taken as the minimum detectable quantity. Using the equation for parts per million (see page28), the peak height values could be substituted along with typical values for other quantities e.g. 100 gm wt. of soil, and 1 ul sample injection volume, to arrive at a detection limit of 0.001 ppm for soil samples. The limit of detection for sediment and water samples was obtained by the same method as above and was found to be 0.0001 ppm. An explanation of "noise level" and the "limit of detection" can be best obtained by referring to the work of Tindle et al (1968) and Mattson et al (1970).

The parameters used in the determination of atrazine residues in parts per million had errors associated with them. The term "error" for the purposes of this study must not be considered as an error in the true statistical sense. Errors obtained during the study were either given by manufacturers for their equipment, e.g. syringe injection volume error, or pipette volume error, or balance error, or others were based on errors inherent in several manipulations, e.g. measurement of peak heights. Errors associated with equipment, e.g. microsyringes, or measurements, e.g. ruler measurements of peak heights are summarized in Table 5. Fractional errors for all the parameters studied, and the overall fractional error are also included in this table. For an understanding of overall fractional error, a discussion of this subject can be found in Brinkworth (1971).

Table 5. Values for the estimation of fractional error for soil residues

Parameter	Normal Magnitude		Fractional Error	Overall Fractional Error
GLC sample volume	0.50 ml	±0.010 ml	0.020	
GLC sample weight	100 g	±0.1g	0.001	
GLC injection volume	1.0 ul	±0.025 ul	0.025	0.001
GLC std. peak height measurement	3.0 cm	±0.02 cm	0.007	
GLC sample peak height measurement	2.0 cm	±0.02 cm	0.010	
GLC std. peak quantity	20.0 ng	±0.08 ng	0.004	

Table 6. Atrazine (parts/million) in soil before application of herbicides 1971-1972. Atrazine at different locations Macdonald College Farm.

Atrazine (Parts/million)

Day No.	Sampling Date	Sampling Depth	Locations							
			1A	1B	1C	1D	2A	2B	2C	2D
1	27/5/71	0-10"	N.S.	N.S.	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
		10-20"	N.S.	N.S.	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
0	8/5/72	0-10"	0.008	0.007	0.002	<0.001	<0.001	<0.001	<0.001	0.002
		10-20"	<0.001	0.002	0.002	<0.001	<0.001	<0.001	<0.001	<0.001

N.S. = Not sampled.

<0.001 (parts/million) = limit of detection.

There were trace quantities of atrazine residues in the 0-10" layer in 1972. The major portion of atrazine was found to be in the upper soil layers.

Discussion

Rainfall and temperature are two factors which are important in determining the rate of soil penetration and the persistence of atrazine. The data for soil residues and amount of rainfall for the two sampling years suggest that there exists some relationship between increased rainfall and increased detectable residues. When compared on an annual basis, eight more inches of rain were recorded in 1972 than in 1971. This increased rainfall favoured a greater amount of leaching of the pesticide to the 10" soil layer in 1972 accounting for higher residue values. Figure 5 shows that there was a rainfall peak in September of 1971 which coincided with an increase in residues both in the 0-10" and 10-20" soil layers. Increased rainfall in June 1972 favoured an increase in the amount of detected residues (Figure 5, Table 3). Furthermore, an increase in rainfall throughout the early part of August 1971 followed by an increase in residues (Figure 2) can be explained as a result of the much drier conditions that prevailed when the samples were taken. With increased moisture conditions on day 69, there was an increase in detectable residues.

The question may be asked why was there such a big difference between the residual amounts of atrazine obtained in the two years. The only logical explanation lies in the fact that there were much better moisture conditions in the second year as revealed by the rainfall figures in Table 7. The crop cover and the temperature range were the same in both years, so that volatilization should have been equally affected by the large surface area of the corn leaves, and the close plant spacing.

The moisture conditions in 1972 definitely favoured greater herbicidal activity in the field. When one considers the limited solubility of atrazine, viz. 70 parts per million, the greater abundance of water would be expected to increase the chances of obtaining more in the soil solution. At least two and a half inches of rain were recorded each month in 1972. The low residues of atrazine in 1971 were the result of several factors. Low rainfall, and the consequent low level of soil moisture probably resulted in some reduction of herbicide dissolution and movement in the field, and promoted retention of the herbicide as an adsorbate on the clay particles. This effect was magnified in the Ste. Rosalie clay soil which was between 36 and 58 per cent clay on the MacDonald College Farm.

Table 7. Monthly temperature and rainfall 1971-1972.

Month	Temperature in °F	Year	Rainfall In Inches	Month	Temperature in °F	Year	Rainfall In Inches
May	65.3	1971	1.56	May	67.4	1972	2.32
June	76.3	1971	1.56	June	71.9	1972	5.41
July	78.0	1971	2.50	July	77.7	1972	7.29
August	75.8	1971	3.89	August	71.0	1972	4.10
September	71.5	1971	5.21	September	68.7	1972	2.46
October	60.7	1971	1.26				

The disappearance curve for atrazine residues on a monthly basis (Figure 4) and during sampling intervals (Figures [illegible] and 3) suggest that the rate of atrazine loss varies with time.

In the literature, LeBaron (1970) has pointed out that triazines are quite resistant to leaching in heavy textured soils, and that residues seldom show significant levels below the 8-12" soil layer even when treatment is repeated. Soil residues in the 10-20" soil layer for 1972 seem to be in agreement with this suggestion (Table 6). Cold wintry temperatures, coupled with spring rains did not seem to contribute to the accumulation of residues in the 0-10" soil layer, or even in the lower 10-20" layer in the early part of 1972 (Table 6). The values for atrazine in the 0-10" soil layer in 1971 were very small, varying from 0.057-0.001 parts per million. On the other hand, Bailey and White (1970) are of the opinion that the total amount of rainfall and frequency of received water affect movement of soil pesticides, and that in heavy textured soils atrazine leaches less readily than in lighter soils. Although the soil of the experimental plot was of the heavy clay type, the abundance of rainfall and increased soil moisture content in 1972 favoured the leaching of the pesticide into the 0-10" soil layer. This accounts for the high residue levels that were obtained.

In considering the effect of atrazine applied to the soil, excess rate of application must be distinguished from dosages used in practice. Field studies are usually variable. This, in part, is dependent on soil type and in most cases on environmental factors. The results obtained for residue analysis indicated that if the compound was applied to the soil at dosage of 2½ lb/acre, the amount of the compound which was recovered as its parent molecule was very small. This indicated that persistence of this compound was not very marked. Nevertheless, adequate weed control was attained.

One important point which should not go unnoticed is the inherent ability of the corn plant itself to contribute to the degradation of this compound. Some analyses of plant materials were undertaken and the results obtained revealed that the amount of the parent molecule remaining within the plant itself, e.g., the leaf sheath was negligible. Shimabukuro et al., 1967;1968;1969;1970;1971) have recognized this fact. The nature of the compound itself is a contributory factor in determining its relative persistence. Because of its limited solubility and ability to be adsorbed by clay material, the greater the amount of moisture present, the greater was its herbicidal activity. This is apparent from a look at the rainfall figures during the course of this study (Table 7, Figure 5) where recovery of herbicide residues was correlated with increases in soil moisture which enhanced leaching into the lower soil layers.

RUN-OFF RESIDUES

The values obtained for run-off water for 1971 and 1972 are contained in Tables 8 and 9, respectively, and are very variable. The highest residue value obtained for tile drain No. 4 was in June, one day after spraying. This abnormally high value does not reflect a true picture for run-off residue and appears to have arisen from accidental drift of spray to this particular ditch. The highest value obtained during the course of the sampling year was from the weir on day 116 (Table 8). This was the only value obtained from the weir throughout the entire sampling period in 1971. Apart from day one, when no sample was taken, the rest of the time the weir remained dry. This is very significant, as it indicates that surface run-off from this field was minimal to almost negligible in 1971 and could not have contributed to any great extent to the total residues obtained for run-off water.

The residue values obtained in June and July for tile

Table 8. Atrazine (parts/million) in lake and field run-off water Macdonald College Farm 1971. Atrazine from different locations.

Atrazine (Parts/million)

Day No.	Sampling Date	Locations					Mean
		Tile Drain #4	Tile Drain #5	Lake (N'West)	Lake (S'West)	Weir	
1*	27/5/71	<0.0001	<0.0001	N.S.	N.S.	N.S.	
14**	10/6/71	<0.0001	0.038	N.S.	N.S.	Dry	
21	17/6/71	T	T	N.S.	N.S.	Dry	
36	2/7/71	T	T	N.S.	N.S.	Dry	
49	15/7/71	<0.0001	<0.0001	<0.0001	N.S.	Dry	
61	27/7/71	<0.0001	<0.0001	<0.0001	N.S.	Dry	
69	4/8/71	0.001	<0.0001	<0.0001	T	Dry	
80	15/8/71	<0.0001	<0.0001	0.002	T	Dry	
96	31/8/71	<0.0001	0.002	0.001	<0.0001	Dry	
116	20/9/71	<0.0001	0.001	T	0.001	0.003	
146	20/10/71	<0.0001	0.001	T	<0.0001	Dry	

*Day sampled before herbicidal application. N.S. = Not sampled.

**One day after herbicidal application. T = Trace, represents range 0.0001-0.001 (parts/million).

<0.0001 (parts/million) = An amount less than the detection limit of 0.0001 ppm for a 300 ml volume of water sample.

Table 9. Atrazine (parts/million) in lake and field run-off water Macdonald College Farm 1972. Atrazine from field and run-off water at different locations.

		Atrazine (Parts/million)				
		Locations				
Day No.	Sampling Date	Tile Drain #4	Tile Drain #5	Lake (N'West)	Lake (S'West)	Weir
0*	8/5/72	<0.0001	<0.0001	<0.0001	T	<0.0001
1	24/5/72	<0.0001	<0.0001	<0.0001	<0.0001	Dry
3	26/5/72	T	<0.0001	T	T	Dry
7	30/5/72	<0.0001	<0.0001	T	T	Dry
14	6/6/72	T	T	T	T	<0.0001
21	13/6/72	T	T	T	0.002	T
28	20/6/72	T	T	T	T	Dry
58	20/7/72	T	<0.0001	<0.0001	T	Dry
93	29/8/72	T	T	T	<0.0001	Dry
128	28/9/72	T	<0.0001	<0.0001	T	Dry

*Day Zero represents sampling time before herbicidal application.

T = Trace, represents the range 0.0001-0.001 (parts/million).

<0.0001 (parts/million) = An amount less than the detection limit of 0.0001 (parts/million) for a sample volume of 300 ml of water.

drains 4 and 5 were about the same. Between June and July, no water samples were taken from the two lake sampling areas. However, for a better and more meaningful monitoring study, the lake was sampled throughout the rest of the sampling period of 1971. Sampling was continued in 1972. The greatest amount of atrazine found in tile drain 4 in 1971 was on day 69. The residues remained constant from day 80 until the end of the sampling time (Table 8). The highest value obtained for tile drain 5 was on day 96. This fell to a value which remained constant for the rest of the sampling period.

The highest value for the most northerly part of the lake was obtained on day 96 (Table 8). This decreased steadily until day 116 after which time trace quantities were obtained till the end of the sampling year. The highest value for the southerly part of the lake was on day 116. This value decreased until the end of the sampling period (Table 8). The highest residue in 1972 was on day 21 (Table 9), but this was lower than some figures obtained for 1971.

Unlike the previous year, trace quantities of atrazine were obtained from day 14 to day 128 in 1972. No residues were detected for tile drain 5 from day 1 to day 7. Trace quantities were obtained from day 14 to day 28. There was then a decrease in residue levels on day 58 with a subsequent rise on day 93, followed by a decrease till the end of the sampling period. Trace quantities for the northerly part of the lake were obtained during all sampling intervals save on days 1, 58 and 128. The highest value obtained for the southeastern part of the lake was on day 21 (Table 8). Trace quantities of atrazine were obtained there on all sampling dates except days 1 and 93.

The weir remained dry throughout the entire sampling period save day 21 (Table 9). This was consistent with what was observed in 1971. Concentration of residues in parts per million plotted against sampling days in the first year are shown in Figure 6. A similar plot of concentration residues in parts per million against sampling days was made for the second year (Figure 7).

An attempt was made to determine the total amounts of residues which were present in any given month. These values were arrived at by totalling the residues obtained for each of the four sampled locations, at each sampling period for the particular month and expressing them as monthly totals versus total amount of residues for the year. The frequency distribution of water run-off residues versus monthly totals for the years 1971 and 1972 are indicated in Figures 8 and 9, respectively.

The histogram for 1971 shows that the highest concentration of residues was obtained in August in all sampling

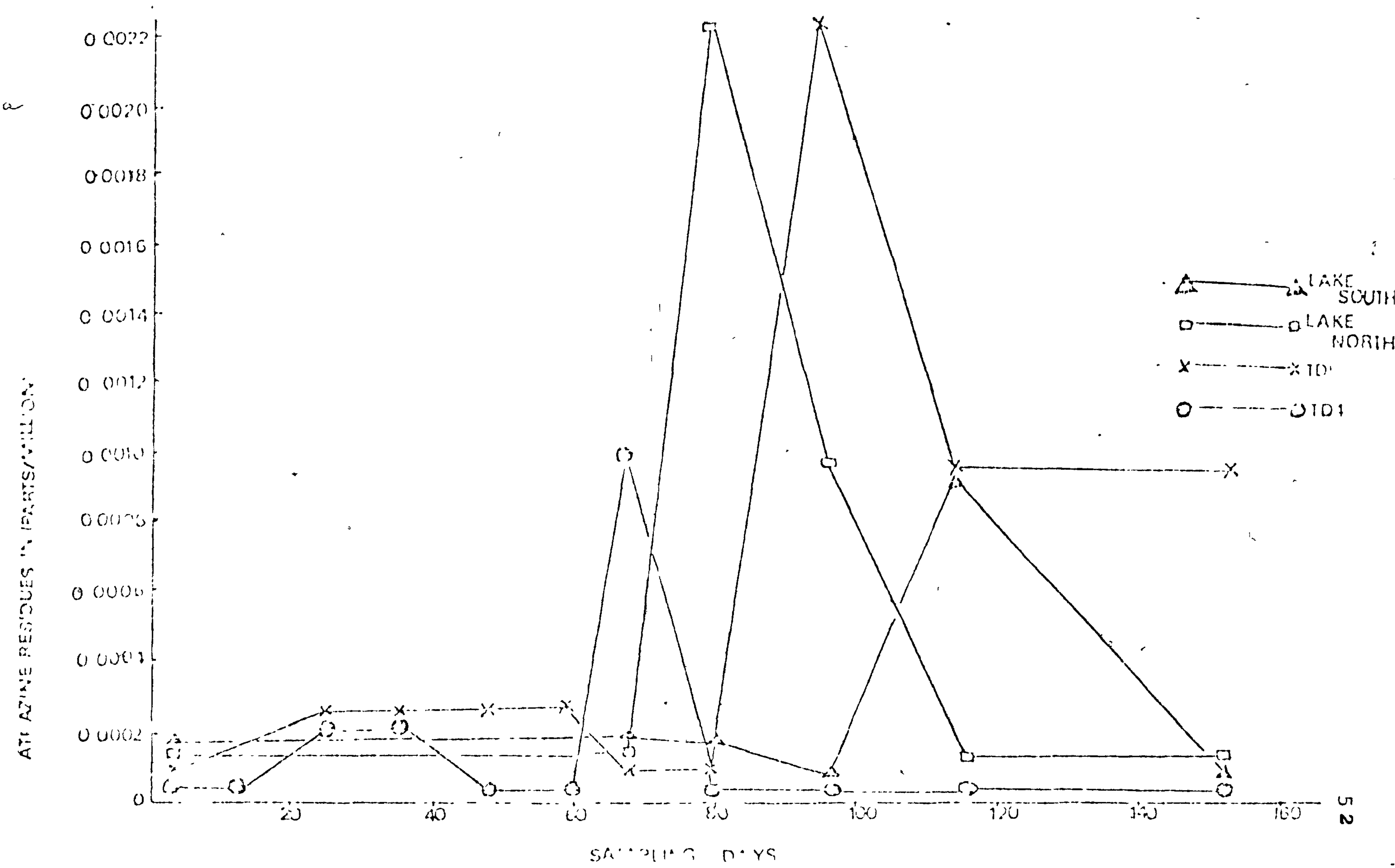

Figure 6. Run-off residues (atrazine) Macdonald College Farm 1971.

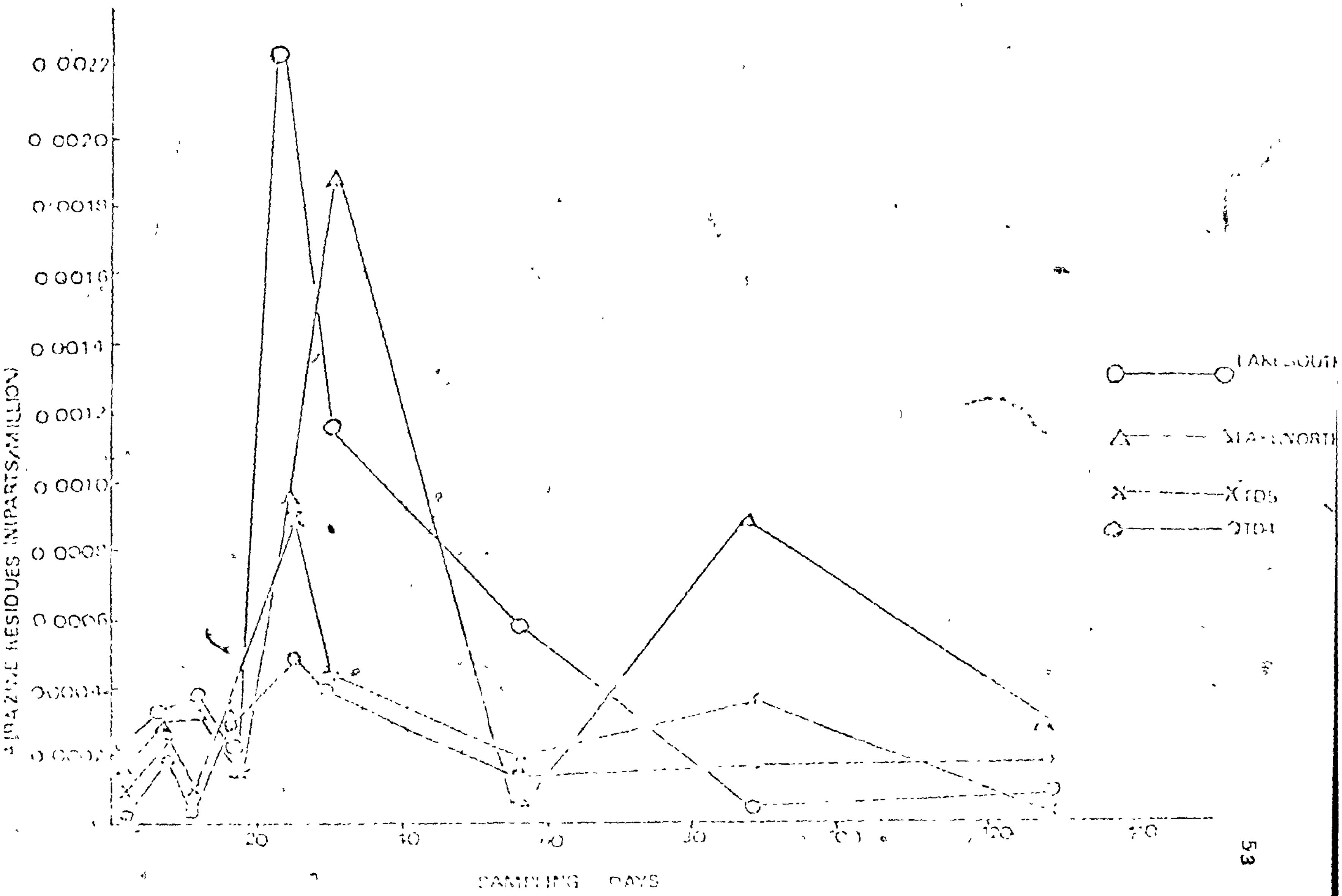

Figure 7. Run-off residues (atrazine) Macdonald College Farm 1972.

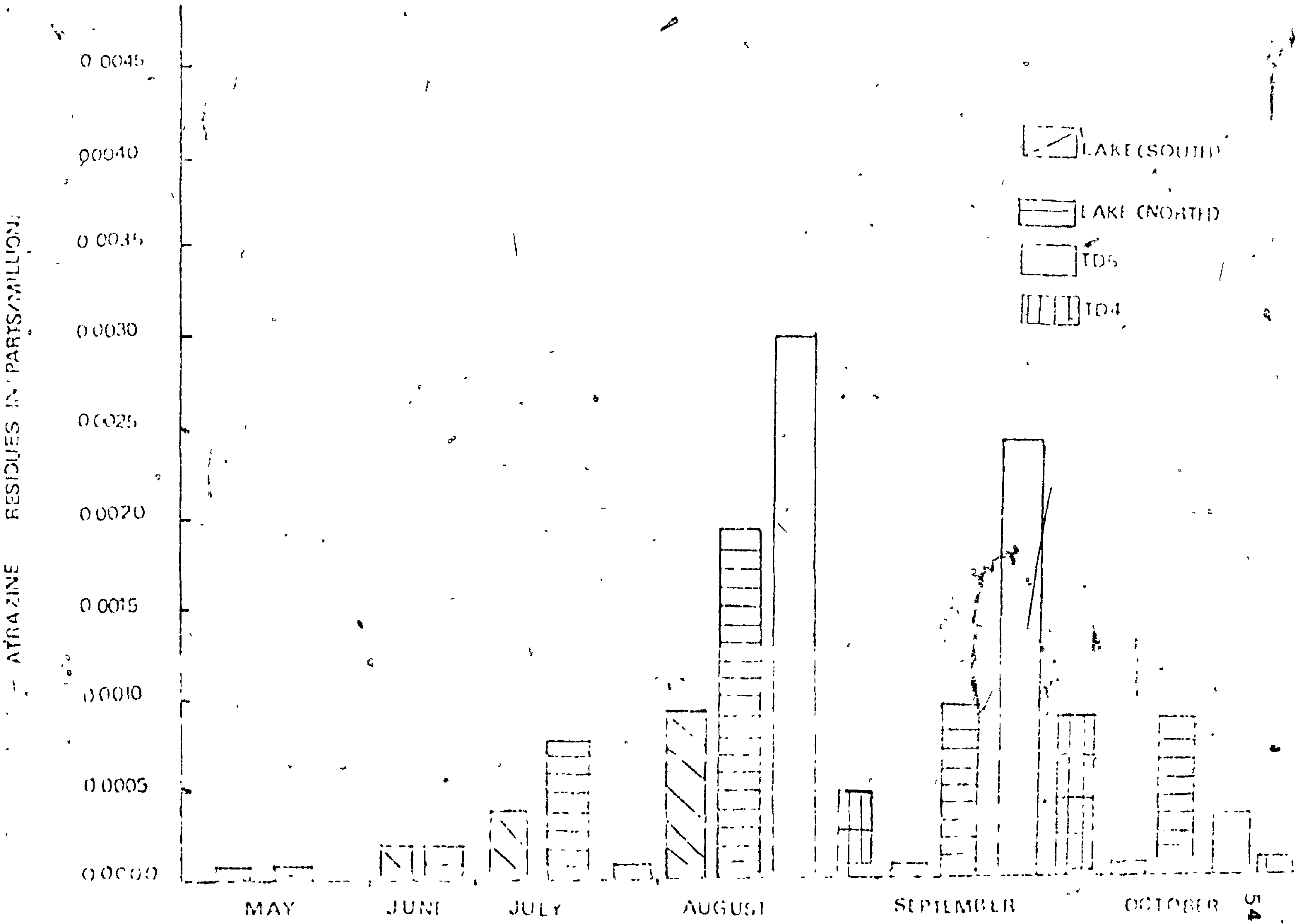

Figure 8. Frequency distribution of atrazine residues in run-off water 1971.

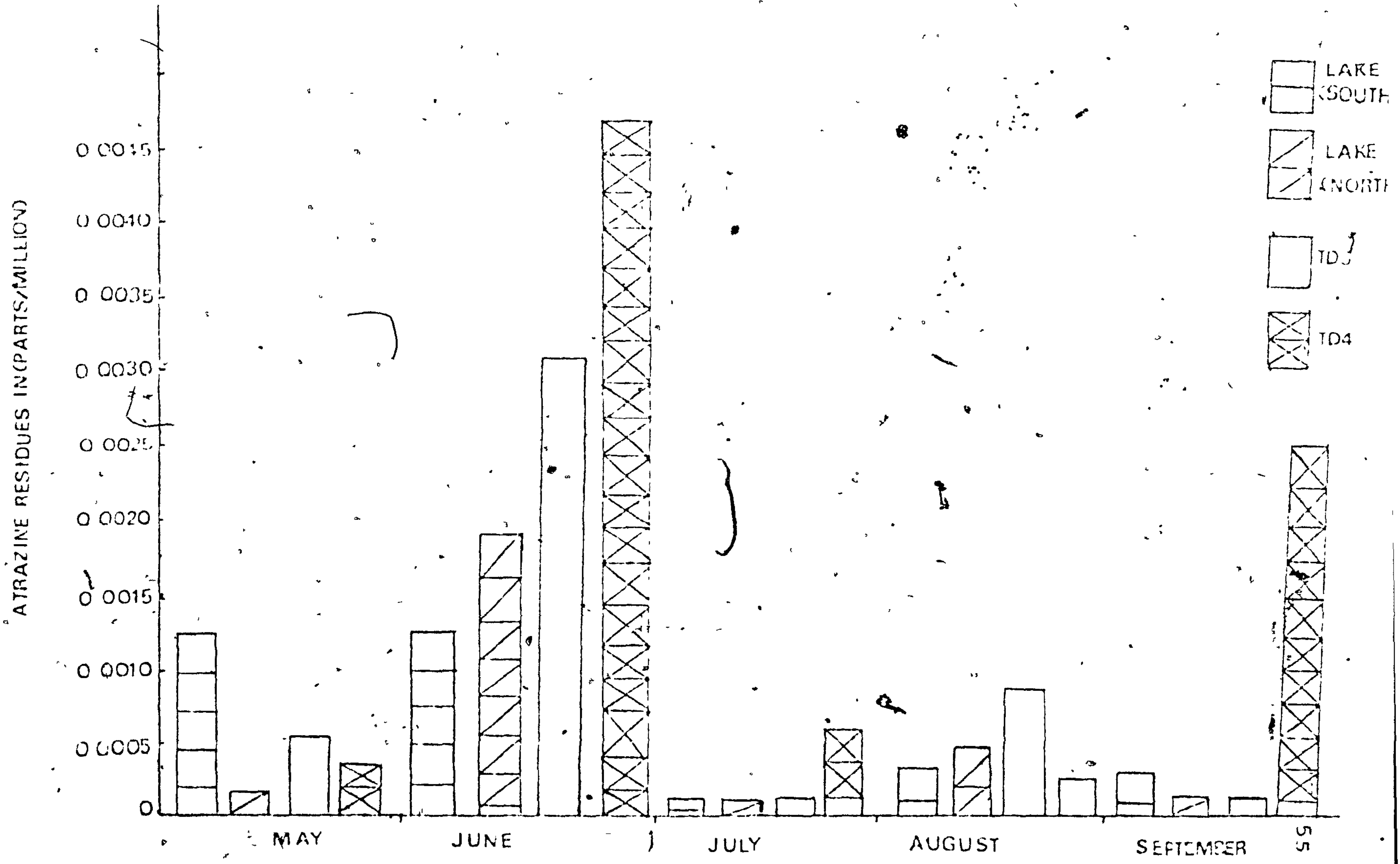

Figure 9. Frequency distribution of atrazine residues in run-off water 1972.

areas. This was followed by high concentrations for three sampling areas in September (Figure 8). Unlike 1971, when the highest concentration of residues was obtained in August, the histogram for 1972 shows that the highest residue concentration was obtained in June in all sampling areas.

Discussion

There was a much greater recovery of residues from all the sampling areas in 1972 than in 1971. Perhaps this can be explained by a look at the rainfall figures for 1972 (Figure 5). The amount of rainfall which was recorded in June was 5.41 inches. This value coincided with the highest amount of detected residues for the month of June in all sampling areas (Figure 9). This high amount of rainfall caused greater pesticide penetration into the lower soil layer and hence its presence in run-off water. Since atrazine is limited in its solubility, the more abundant rainfall increased its dissolution in the soil water and thus affected its transportation in run-off water. The recovered amounts of residue are not very high. Possibly soil type contributed to controlled percolation into the lower soil layers resulting in a very slow and low accumulation of residues in soil water and hence in run-off. This in effect could account for the surprisingly low values obtained for tile drains 4 and 5 for the months of July, August and September, particularly when rainfall was highest in July.

An explanation may lie in the fact that most of the pesticide present in run-off water from the field had been either converted into one of its metabolites and hence was not present as its parent molecule, or in the fact that run-off was so great that any residues present were quickly transported to the lake, since the tile drains had overflow openings into the lake.

The values obtained for the lake sampling areas can be explained by the fact that spring rains enhanced run-off which resulted in very large amounts of atrazine being transported to the lake. This is reflected in the value obtained for June (Figure 9). September was a peak residue period for the lake residues accumulated over a period of time in lake waters. The highest concentration of residues (Figure 9) was found in the southeastern portion of the lake. This area represented the extreme corner of the lower portion of the lake where the water was relatively undisturbed, and atrazine, because of its limited solubility accumulated. The rate of atrazine loss due to water, in 1972 (Figure 7) decreased with time in all of the sampling areas. This is consistent with the pattern of disappearance that was obtained for soil residues. The increase, on day 93, in the northwest portion of the lake and tile drain 4 could have been due to greater herbicidal activity of the compound as a result of very high rainfall in the previous month making this compound readily available in the soil solution. Just as in 1972, a similar period of high rainfall in 1971 coincided with a high amount of detected residues (Figures 7 and 5).

High values were obtained for all sampling areas in August. This was particularly true for the northwestern portion of the lake. This was brought about by the greater abundance of water towards the end of July, which increased the amounts going into solution and promoted percolation to the lower soil layers and subsequent transportation in run-off water. The peak periods of residues in September can also be explained by the greater abundance of moisture. The low residue values obtained for June are not surprising since there was only one and a half inches of rainfall during that period. The heavy clay type soil seriously hampered or even totally prevented penetration to the lower soil layers. Sheets (1970) has suggested that the activity of atrazine is very limited under dry conditions such as occurred during the month of June in the first year. Dry conditions promoted adsorption onto the heavy clay material, thus restricting availability, and hence the absence in run-off water.

The rate of loss of atrazine in 1971 (Figure 6) as in 1972 (Figure 7) decreased with time. The peak periods for residues correspond to the peak rainfall periods. There was a decrease in residue values with increased time for all the sampling areas, save the southeastern portion of the lake. The rise on day 116 is correlated with the greater abundance of run-off in September which favoured an accumulation of atrazine residues in a portion of the lake which was relatively stagnant. Since the weir remained relatively dry throughout the two years of sampling, it appears obvious that surface run-off did not influence the residual concentration of the herbicide. The run-off water which carried the atrazine percolated through to the lower soil layers and then out into the tile drains. The tile drain outlets from the field fed tile drains 4 and 5 which were situated four to five feet below the soil surface.

Pesticides distributed in the environment are rarely uniformly dispersed. Soil residues may be either carried out by surface run-off water from fields, or be leached into ground water supplies. Run-off water from agricultural fields can undoubtedly contribute to the contamination of lakes or water reservoirs. The degree of contamination seems, however, to depend on the nature of the compound used, its rate of application, the availability of water, and the nature of the soil type.

In the course of this study, the amount of recovered residue was not alarmingly high. This was contributed to by the inherent ability of the parent molecule to degrade steadily with time, and thus not appear in the water source to any great extent in its original form, and by its limited solubility which resulted in a high proportion of the material being adsorbed onto the soil particles which held it against leaching.

Kenaga (1972) contends that the water solubility of a pesticide is of key importance in governing its behaviour in any environment. It can in fact determine its persistence or disappearance. During the course of this study, the degree of water solubility definitely influenced the amount of atrazine which was recovered. This is reflected in Figures 7 and 9, where there were definite correlations between residue accumulation in run-off water and periods of rainfall abundance.

Biological factors can influence molecular transformation of a pesticide and thus influence its residual accumulation. Atrazine can be converted into some of its water soluble metabolites in the environment. The resulting rapid rate of disappearance renders any monitoring study for the quantification of residues difficult.

SEDIMENT ANALYSIS

The data obtained for the analysis of sediment material from all sampling areas are presented in Table 10. Sediment material was not sampled before soil treatment. Day zero was considered as the day before application of the atrazine. Table 10 shows that the highest concentration of atrazine was obtained from tile drain No. 4 on day 128. Concentration of residues expressed in parts per million, plotted against sampling days are presented in Figure 10. Monthly amounts of residues plotted against months of sampling are presented in Figure 11.

Discussion

The residue obtained in the lake bottom sediment was low. This is surprising, since there is a natural tendency for pesticide residues transported in run-off water from agricultural fields to accumulate in lake bottom sediment. This has been recognized by Edwards (1970) and Eichelberger *et al.* (1971). High levels of detectable residue in the sediment did not coincide with peak periods of rainfall as was observed for residues in soil water. Perhaps the parent

Table 10. Atrazine (parts/million) in sediment on Macdonald College Farm 1972. Atrazine from different locations.

Atrazine (Parts/million)

Day No.	Sampling	Locations Tile Drain #4	Tile Drain #5	Lake (Northwest)	Lake (Southwest)
1	24/5/72	<0.0001	<0.0001	<0.0001	<0.0001
3	26/5/72	<0.0001	<0.0001	<0.0001	<0.0001
7	30/5/72	0.002	0.002	T	<0.0001
14	6/6/72	<0.0001	<0.0001	<0.0001	<0.0001
21	13/6/72	<0.0001	<0.0001	<0.0001	<0.0001
28	20/6/72	<0.0001	<0.0001	<0.0001	<0.0001
58	20/7/72	0.002	<0.0001	<0.0001	<0.0001
93	29/8/72	<0.0001	<0.0001	<0.0001	<0.0001
128	28/9/72	0.004	0.002	0.002	0.001

T = Trace, represents a range of 0.0001-0.001 (parts/million).

<0.0001 = An amount less than the limit of detection of 0.0001 (parts/million) for 100 g of sediment.

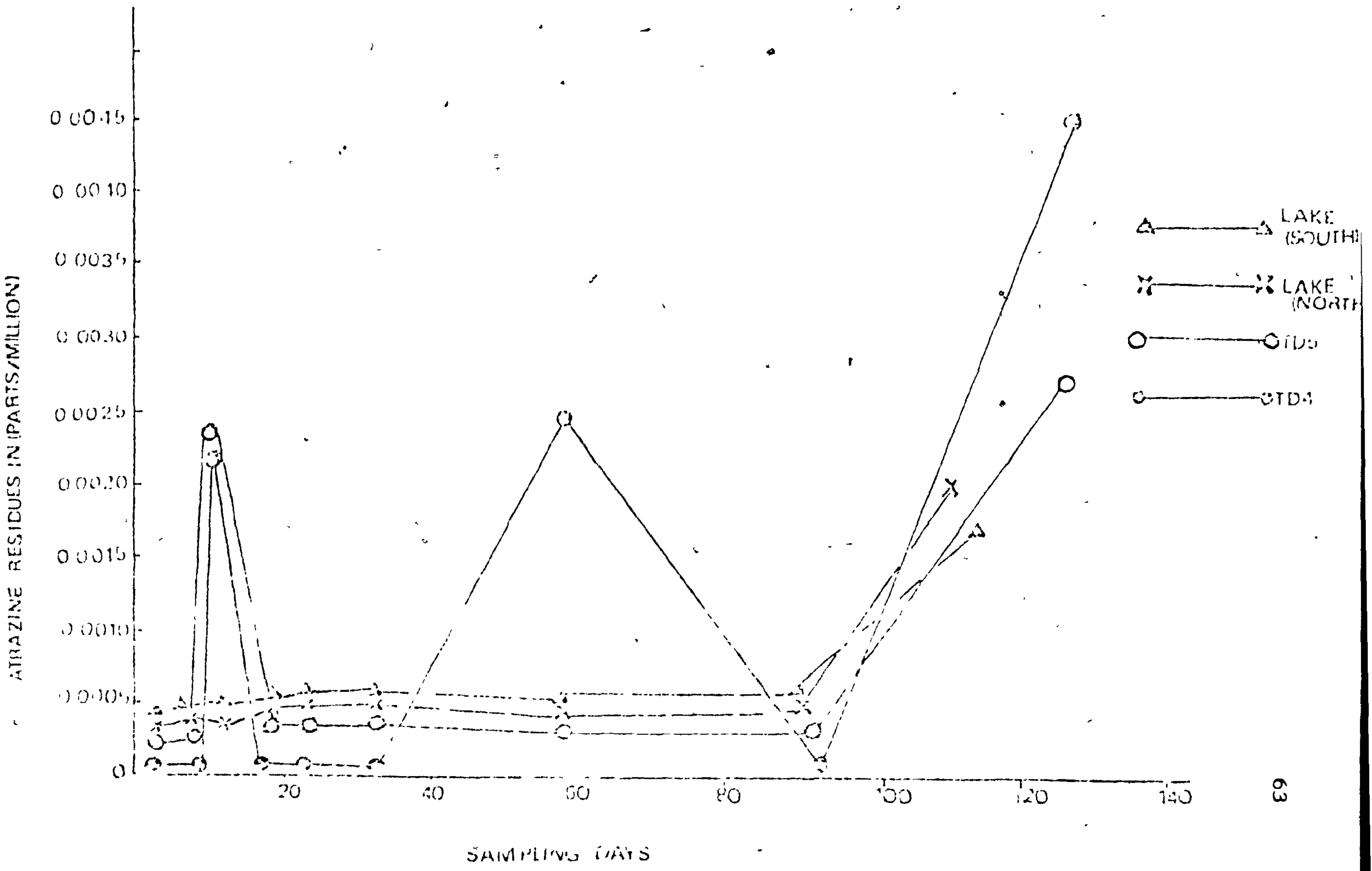

Figure 10. Atrazine residues in lake sediment Macdonald College Farm 1972.

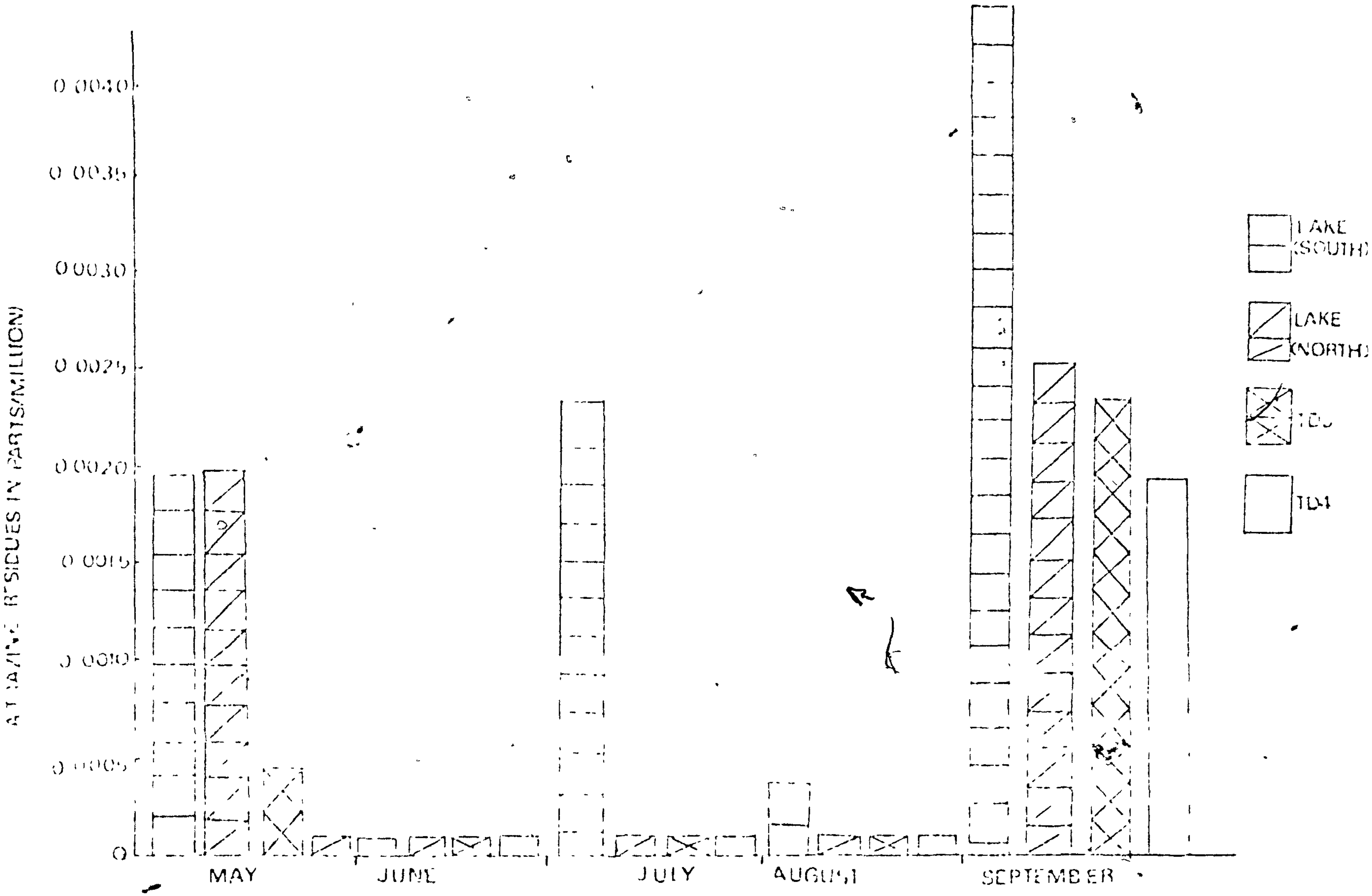

Figure 11. Frequency distribution of atrazine residues in lake bottom sediment 1972.

molecule was either converted to one or more of its water soluble metabolites, and hence was not detectable by the methods used, or perhaps microbial degradation of the parent compound occurred in the lake bottom.

Because of the limited solubility of atrazine and the high clay content of the soil, vertical leaching to the lower soil layers and hence release into the soil solution was a slow process. Slow movement in the lower soil layers eventually resulted in transportation into run-off water to the tile drains and the lake water. As the amount of residue in the lake water increased, precipitation of the atrazine residue to the lake bottom also increased. This eventually resulted in the detectable amounts of residue towards the end of the sampling period.

GENERAL DISCUSSION AND CONCLUSIONS

Problems arise following repeated application of atrazine when highly sensitive crops are grown in rotation with corn. This was reported by Frank (1966) for sugar beet. Soil carry-over residues of atrazine depend on the rate of application. Roadhouse and Birk (1964) showed that an application of 2½ lb/acre of atrazine to a soil on which corn was planted did not result in injury to barley grown on this same soil afterwards. However, at an application rate of 10 lb/acre crop injury resulted.

During the two-year study reported here, an application rate of 2½ lb/acre was used. Adequate weed control in the crop was obtained, with negligible soil carry-over residues. However, the influence of rainfall, soil type, and of the corn crop itself on loss of soil residue was appreciable, and suggests that dosage and sensitivity of the follow-up crop might not always be adequate criteria for prophesying safe residue levels.

The methods of analysis used in the course of this study were concerned with the detection of the parent molecule in the soil environment. The effect of the parent molecule on soil microflora and its microbial degradation has been investigated by Kaufman (1964), McCormick et al. (1966) and Fink et al. (1968). Investigation of the role of atrazine metabolites in the environment appear to have been confined to the metabolites found in the corn plant (Shimabukuro et al., 1967,1968,1971; Lamoreux et al., 1970,1972). The soil is a heterogenous mass and as a result of its complexity, the interplay of environmental factors can affect or influence the activity of a particular pesticide in the field. There is still need for further research on the effect of the metabolites of atrazine on the soil environment.

Many of the investigations reported in the literature have been adsorption and desorption studies of atrazine in various soil types, e.g. studies of the leaching and movement (Burnside et al., 1963; Talbert and Fletchall, 1964; Bailey and White, 1970). Such studies, although they appear to offer an explanation and possible demonstration that this pesticide has limited solubility, do not provide information that can be used to predict either adsorption onto the soil, onto lake sediment or transportation in field run-off water. In order that experiments with atrazine may be more useful, future work should be focussed on the measurement of adsorption, desorption, rather than inferring them from observations based on the distance of travel of this pesticide in soil layers in leaching experiments, where water relations are uncontrollable and usually unpredictable.

Helling (1970) has suggested that the possible routes towards environmental contamination by pesticides include vertical leaching to ground water and surface movement. The low levels obtained for soil, run-off water and lake sediment seem to suggest that this compound does not appear at this moment to impose a serious threat to the environment. The use of atrazine in corn production therefore appears to be advantageous. Adequate weed control in the crop was obtained at a very low rate of herbicidal application. Soil carry-over residues were negligible, while residue levels in field run-off water and lake bottom sediment were low.

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APPENDIX

Table I. Operating parameters for gas liquid chromatography. Alkali flame ionization detector.

Detector	Attenuator Settings (amp/ml)	Chart Speed and Recorder Impedence	Column Packing	Qty. of Pesticide Giving ½ F.S.D.(a)	Gas Flow Rates (ml/min)	Pesticide Retention Time	Column Matl.& Dimension	Oven Temps (0°C)	Theoretical Plates
Cesium	$32x10^{-10}$	1/3"/min	1% OV-lon	80 ng	N_2=30(b)	3 min	5'x1/8"	Column oven	
Bromide	$16x10^{-10}$		Porapack-30	Atrazine	H_2=20(c)		I.D.	=20±1	
(Salt tip)	$8x10^{-10}$	1 Mv impedence	100/120 mesh		Air=180		Brass (on Col sample injector)	Dector= 225±1 injector oven= 225±1	Not Calculated

(a) = Full scale deflection on the recorder chart measured at attenuation setting of 4 x 10^{-10} amps/mv.

(b) = carrier gas (N_2) flow rate measured at column outlet.

(c) = flow rates with the AFID measured at the detector jet.

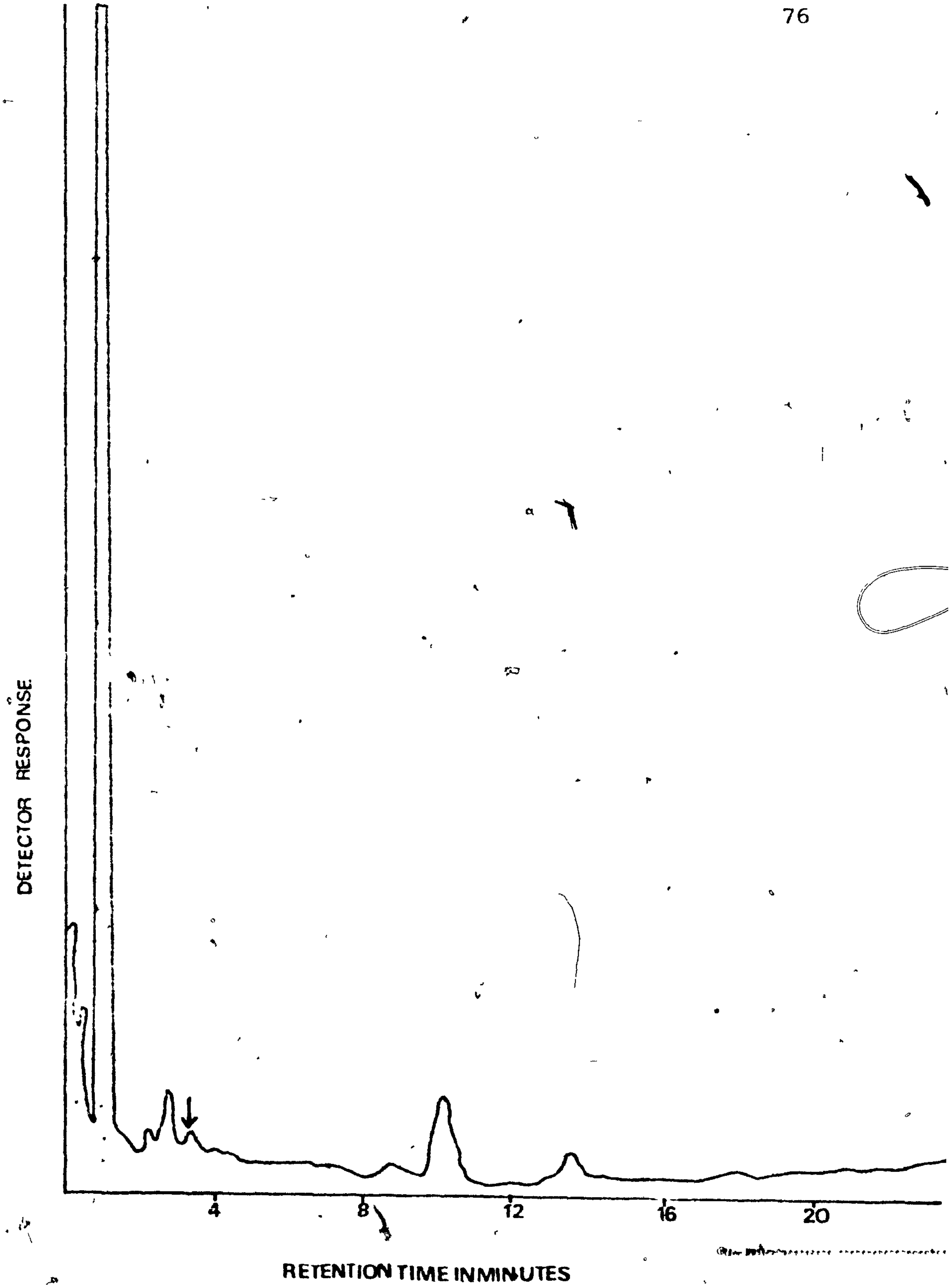


Figure 1. Soil residues - recovery of Atrazine.
IB 10-20", 8/5/72.

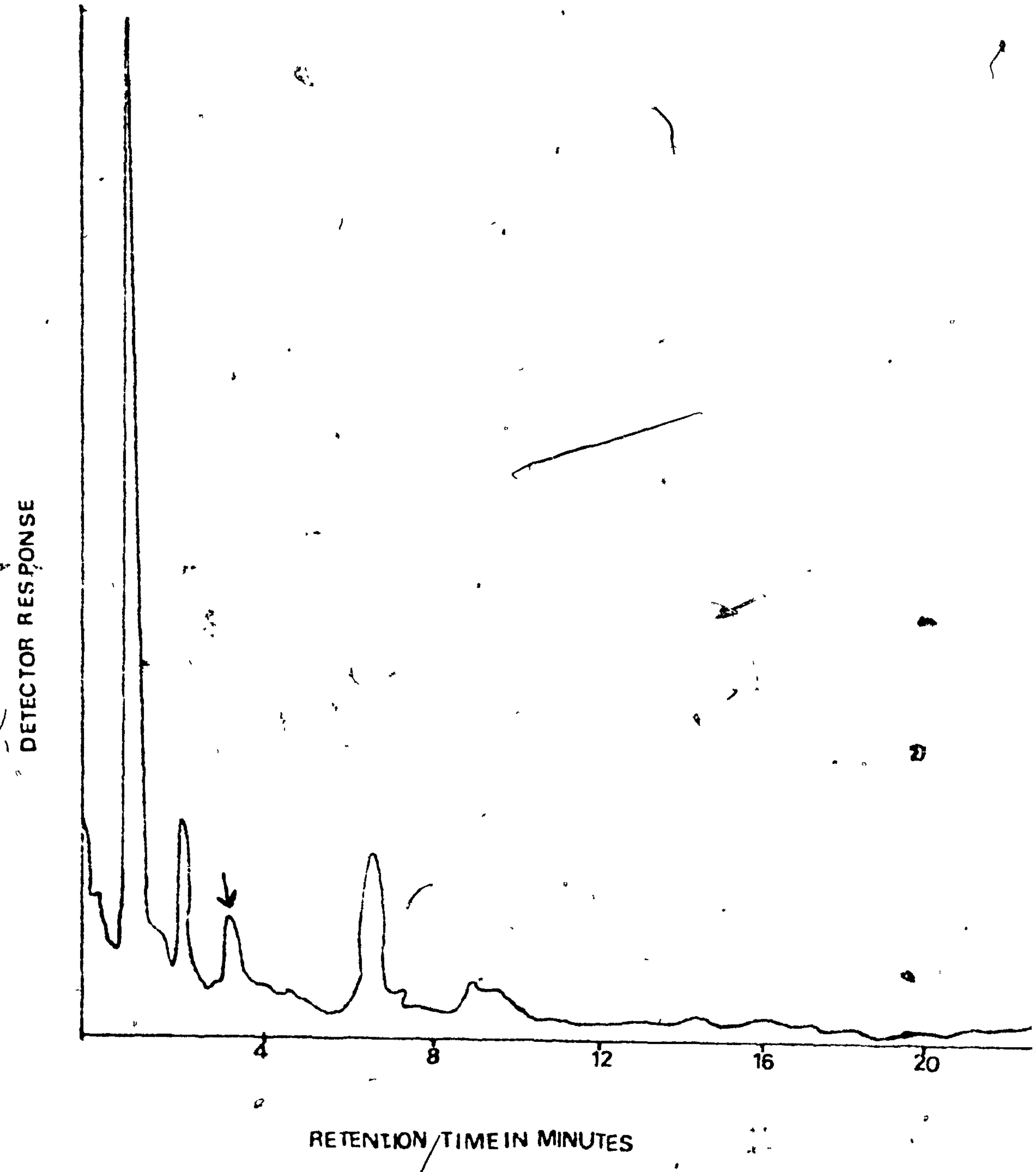


Figure 2. Run-off residues - recovery of Atrazine. Upper Lake, 20/6/72.

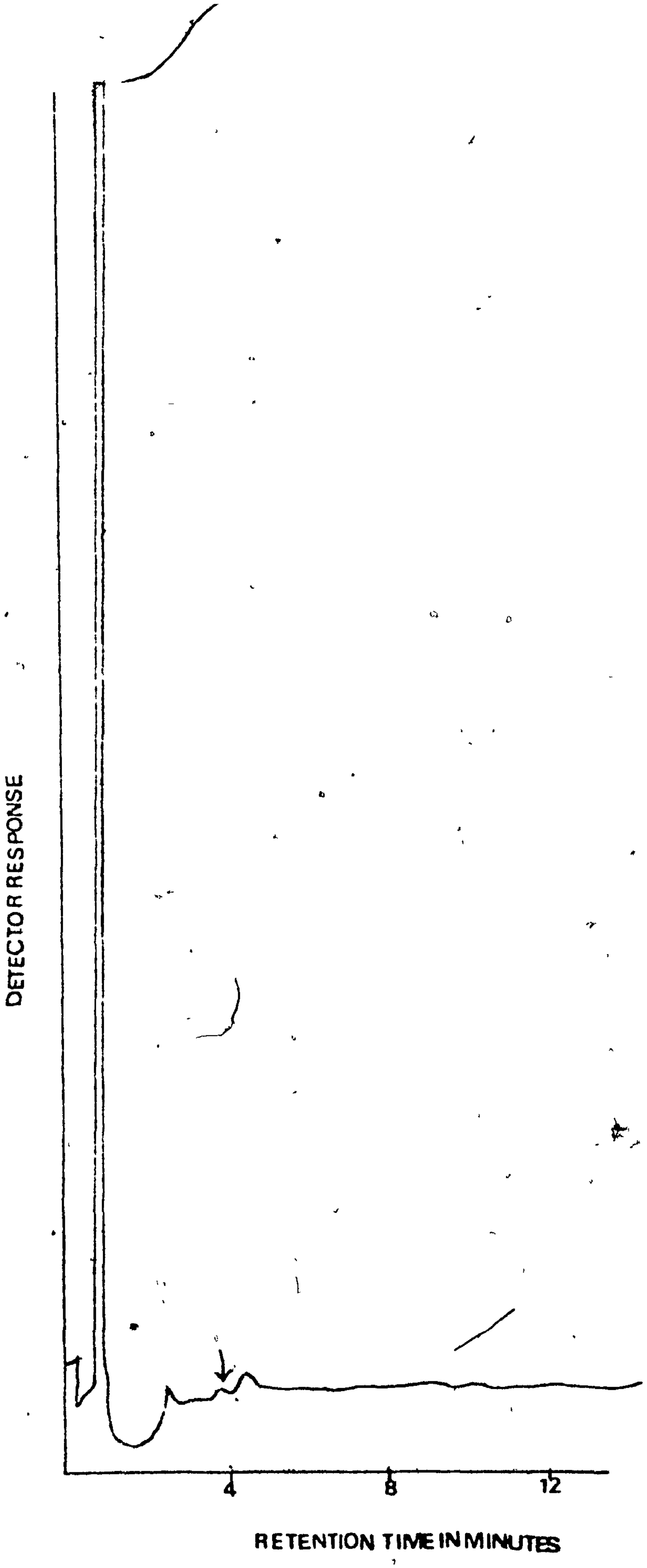


Figure 3. Soil residues - recovery of Atrazine. IB 0-10", 8/5/72.

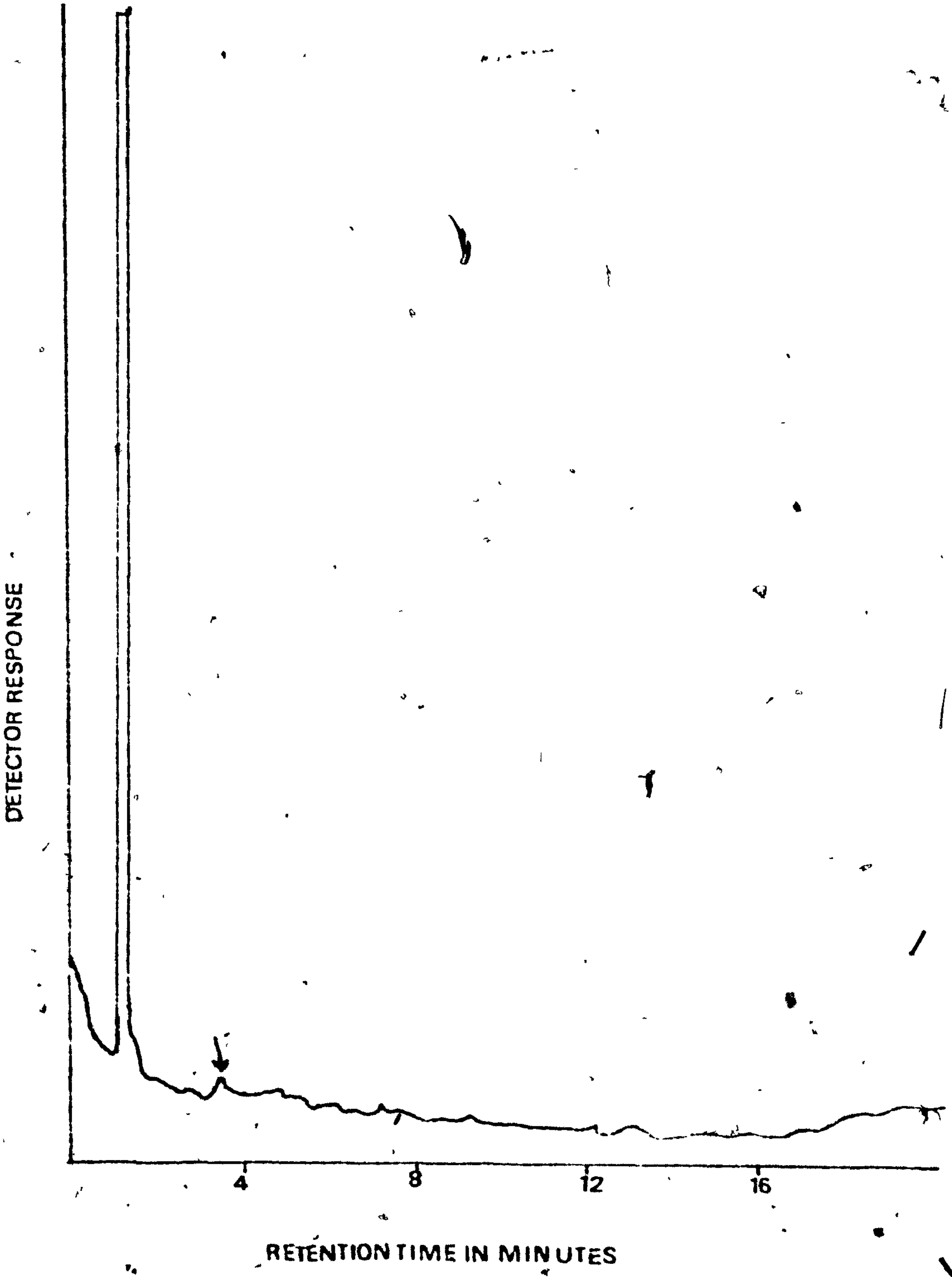
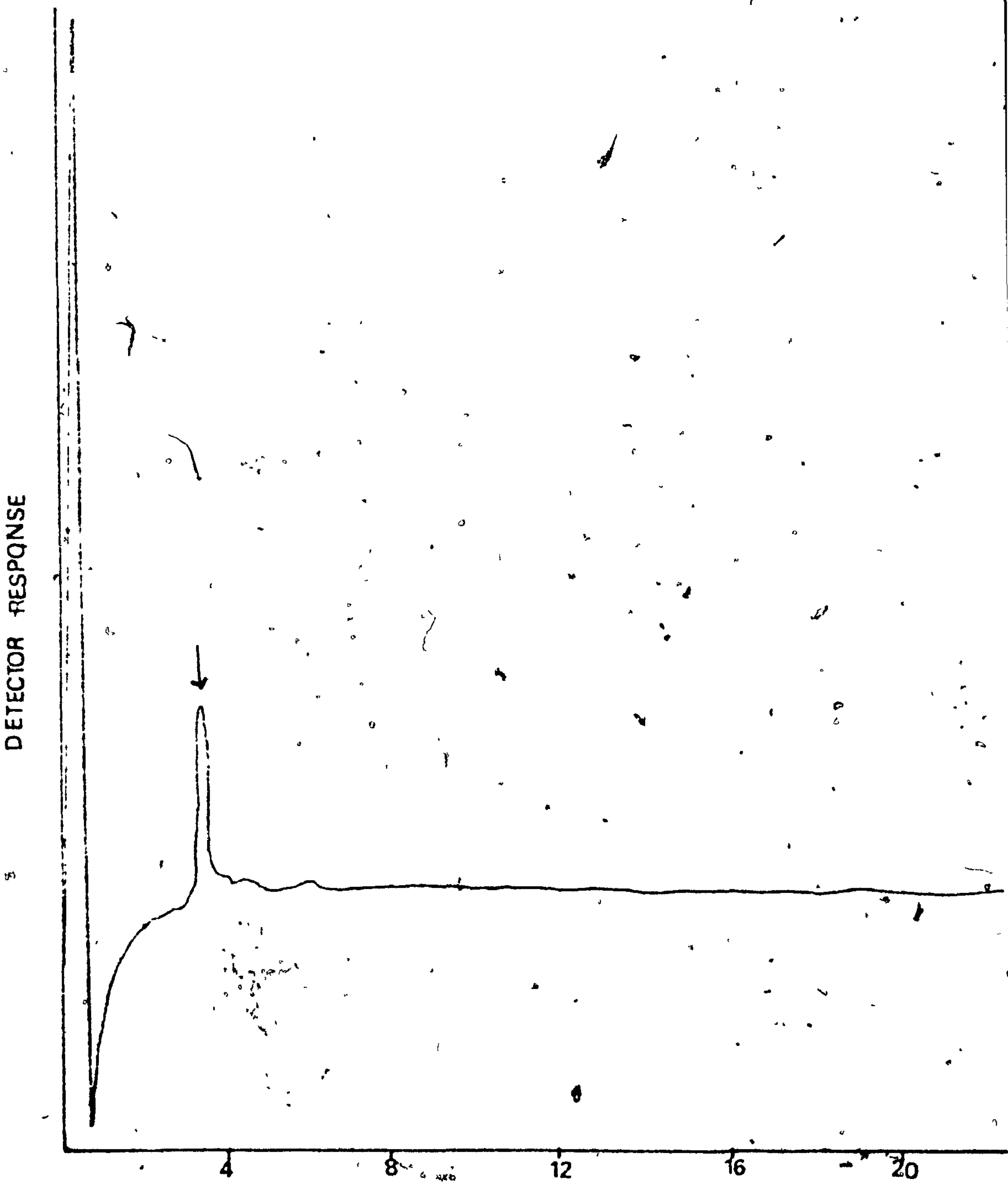


Figure 4. Run-off residues - recovery of Atrazine
TD4, 13/6/72.



RETENTIONTIME IN MINUTES

Figure 5. Atrazine standard. 18.5 ng/ul. 8/1/73.
Retention time = 3 minutes.

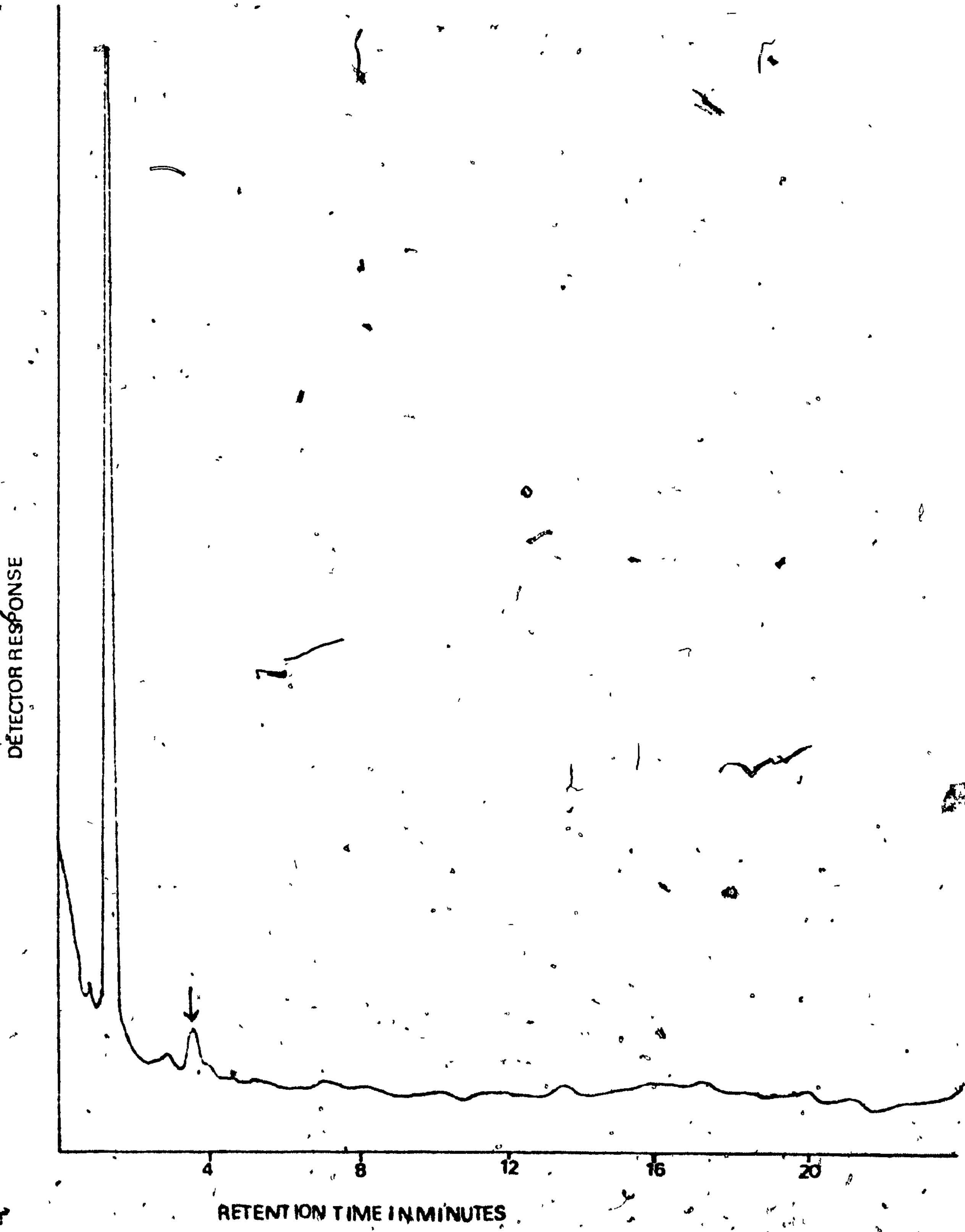


Figure 6. Run-off residues - Recovery of Atrazine. Lower Lake, 20/6/72.

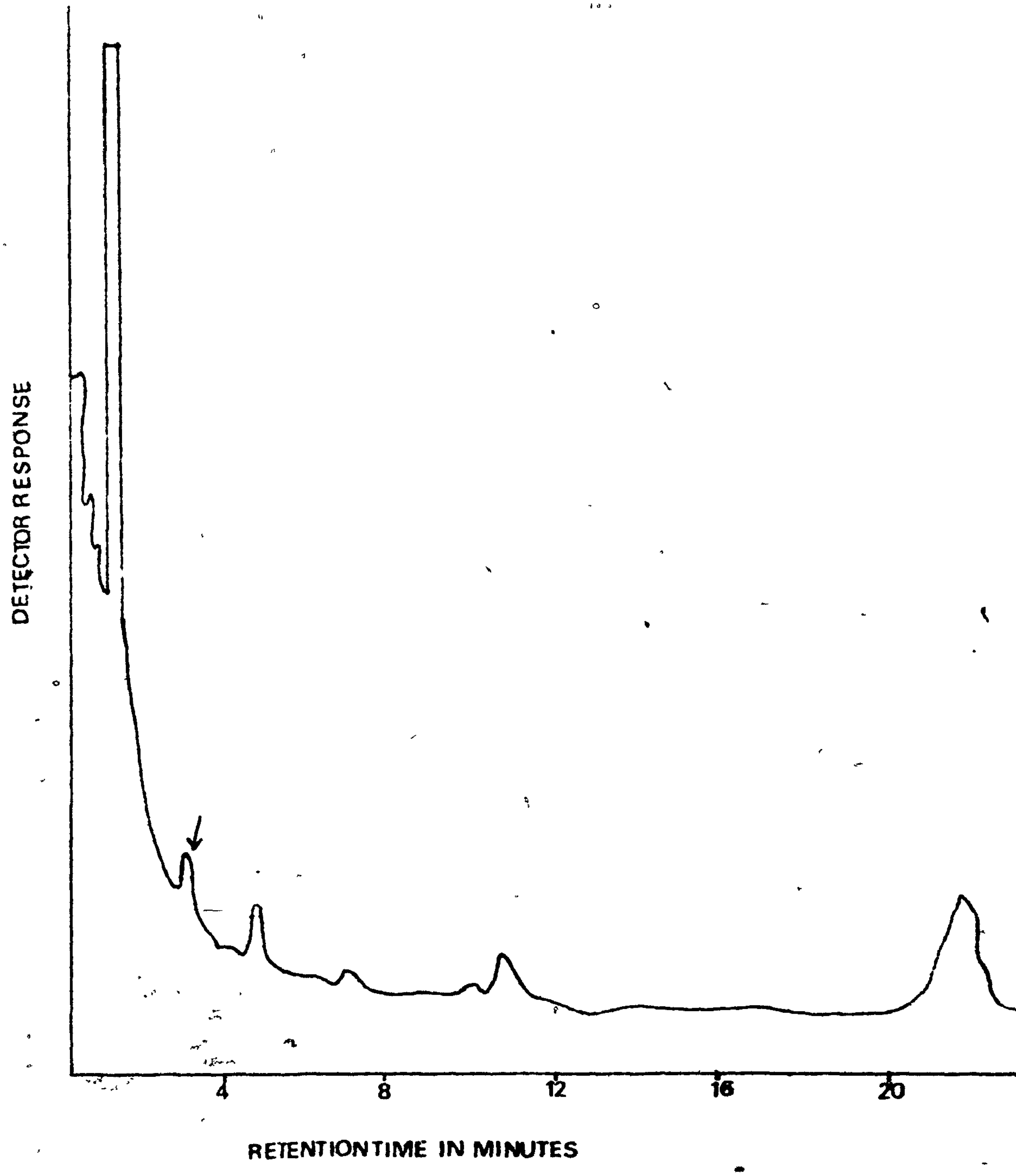


Figure 7. Sediment residues - Recovery of Atrazine. Upper Lake, 28/9/72.

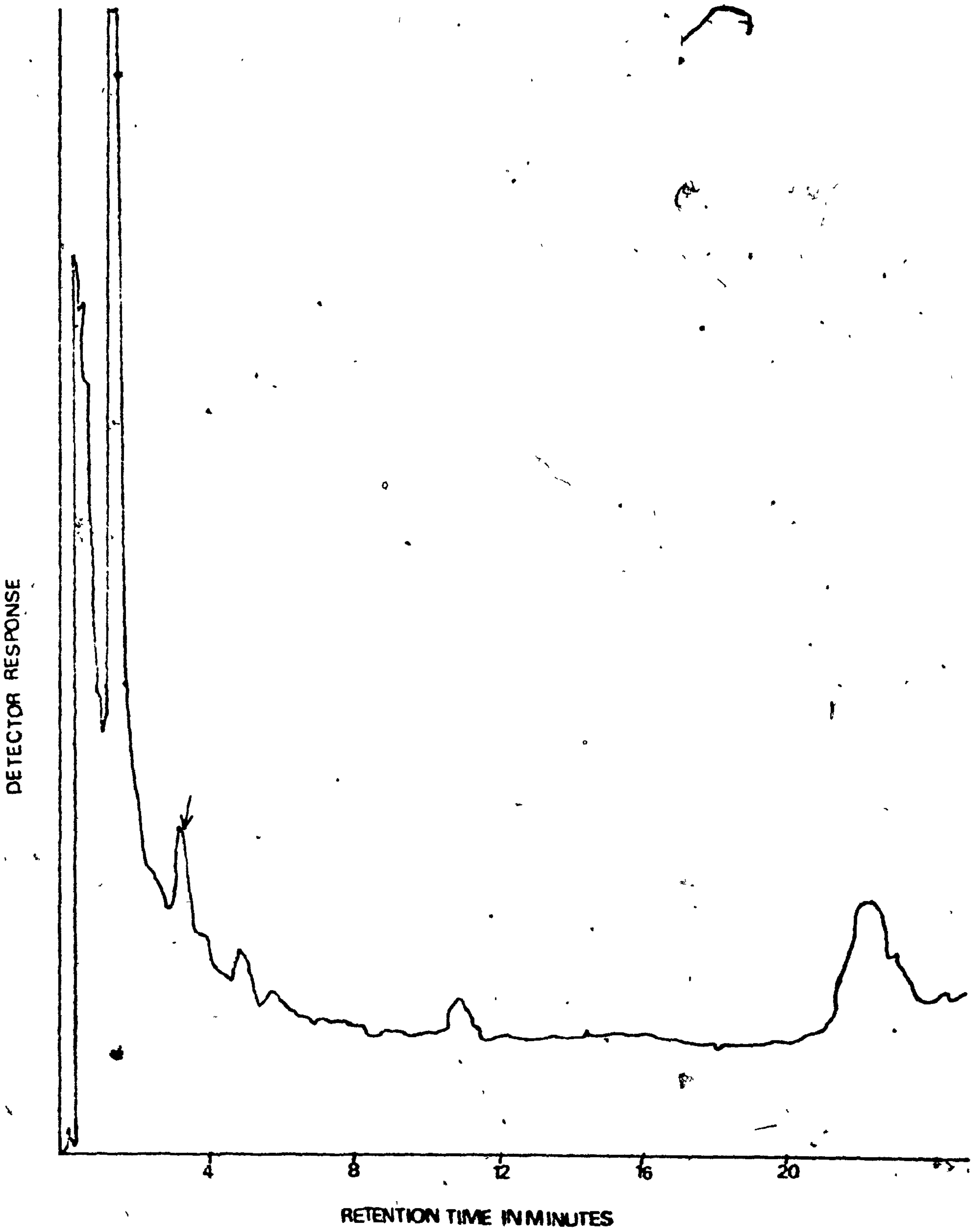


Figure 8. Sediment residues – Recovery of Atrazine. TD4, 28/9/72.

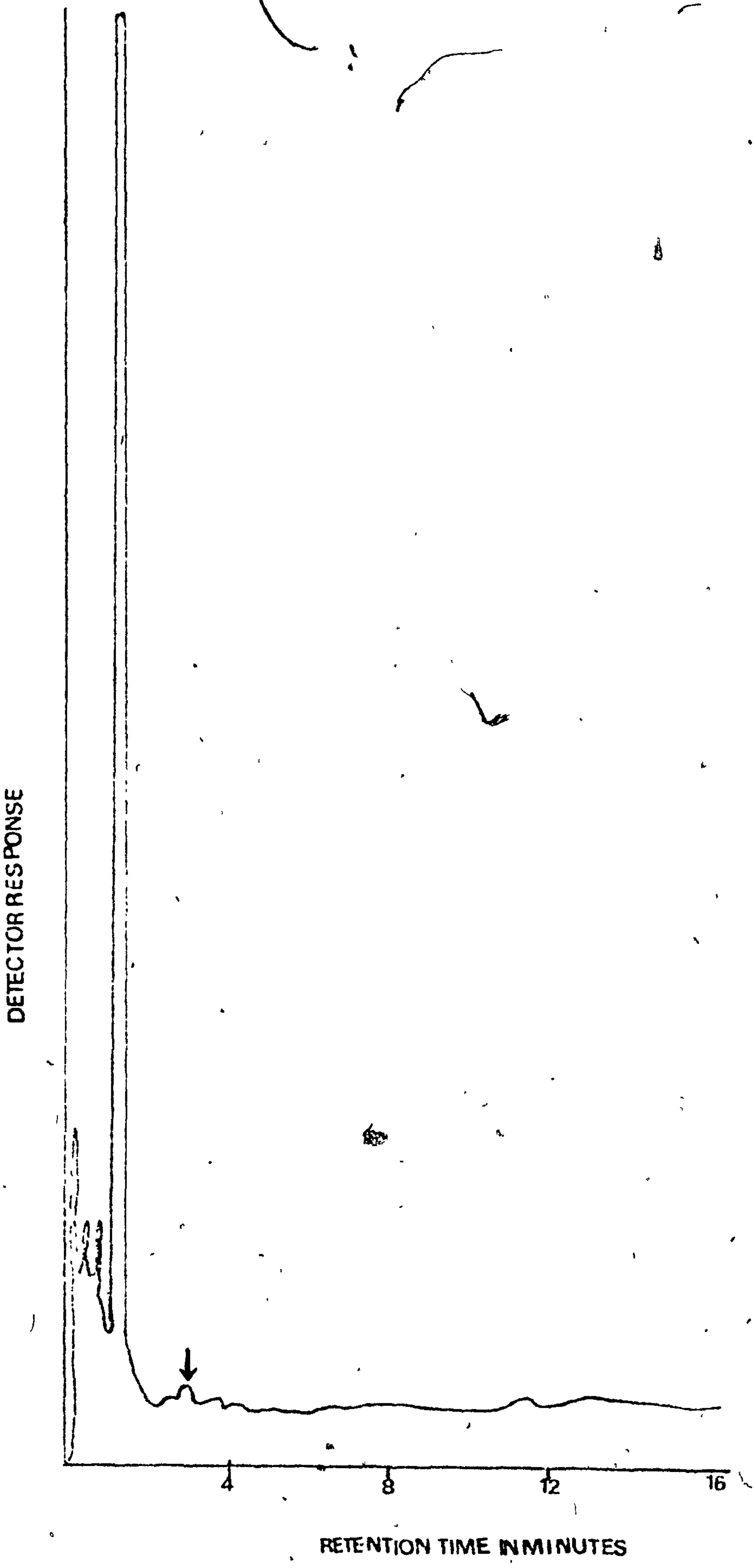


Figure 9. Run-off residues - Recovery of Atrazine.
TD5, 6/6/72.

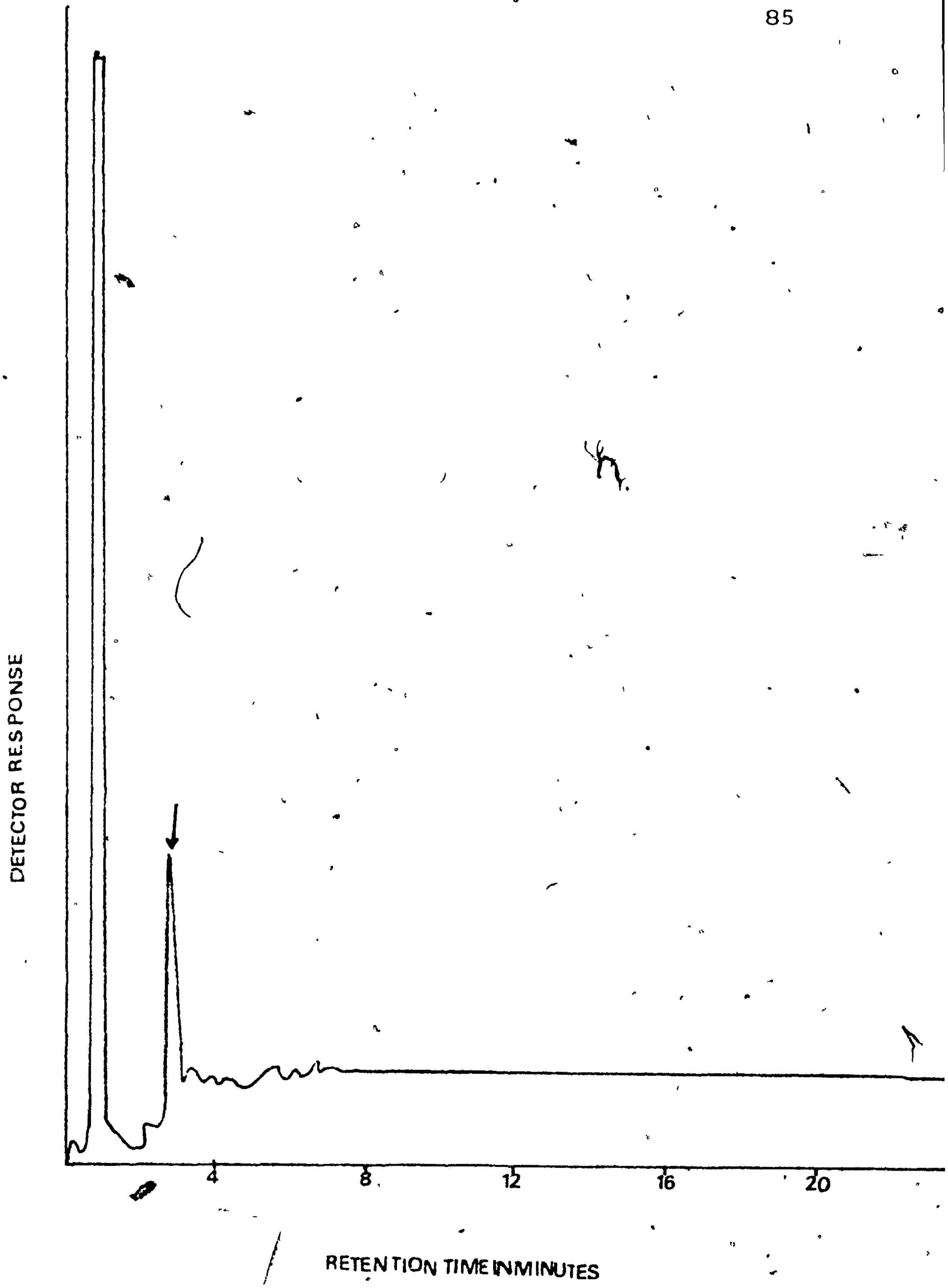


Figure 10. Soil residues - Recovery of Atrazine. A2, 0-10", 6/6/72.

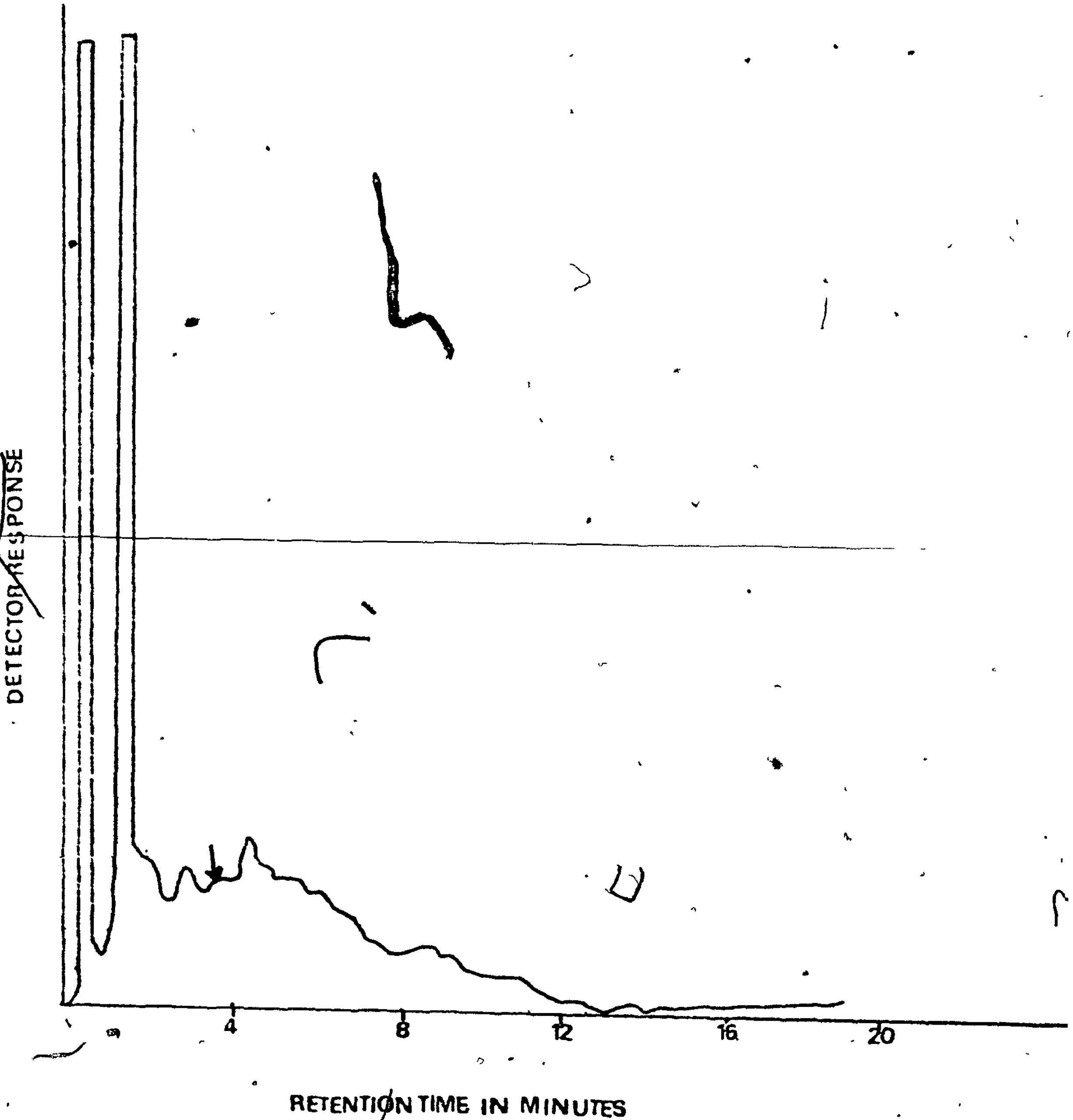


Figure 11. Sediment residues - Recovery of Atrazine. TD5, 6/6/72.

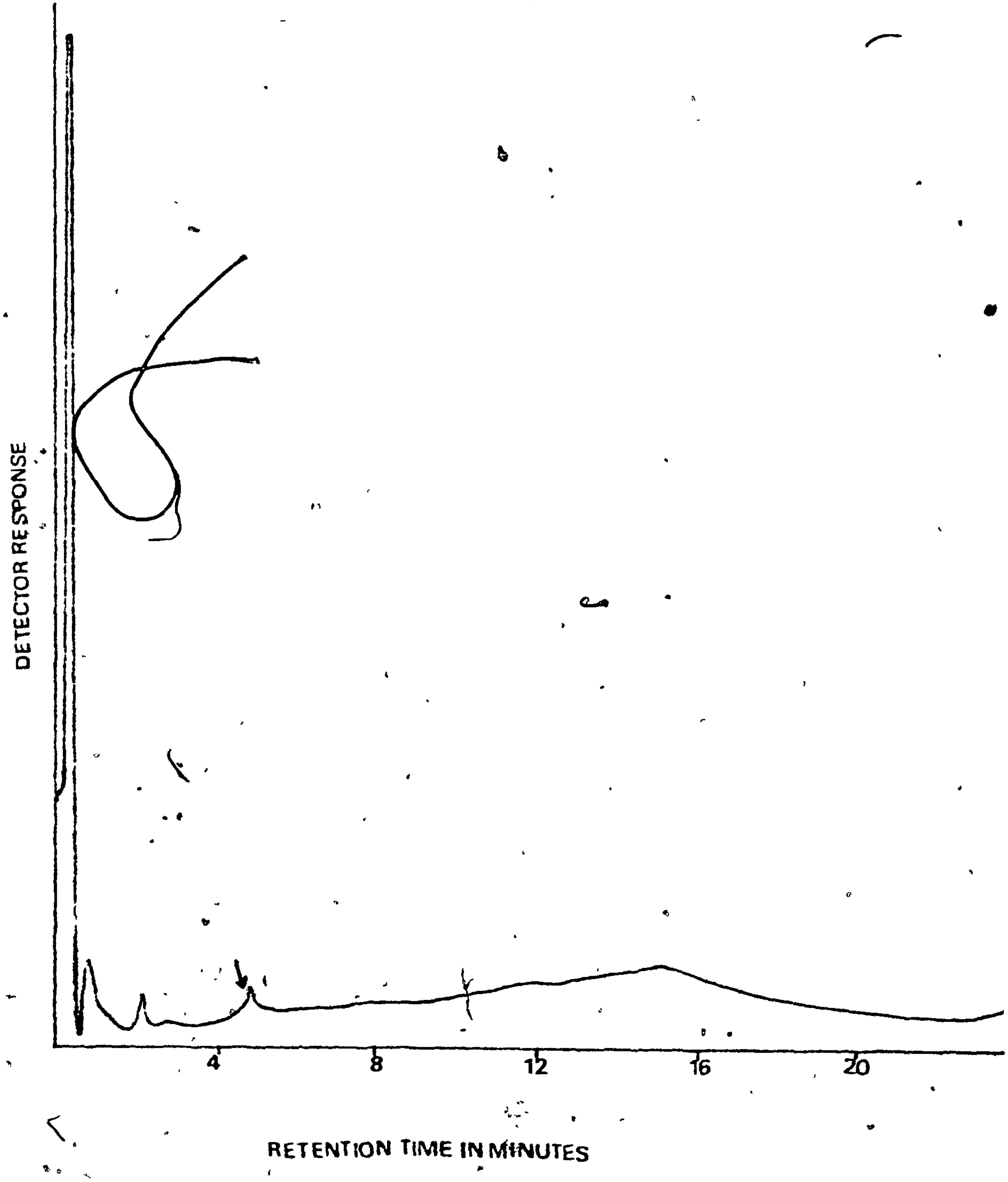


Figure 12. Soil residues - Recovery of Atrazine.
2B, 10-20", 15/8/71.

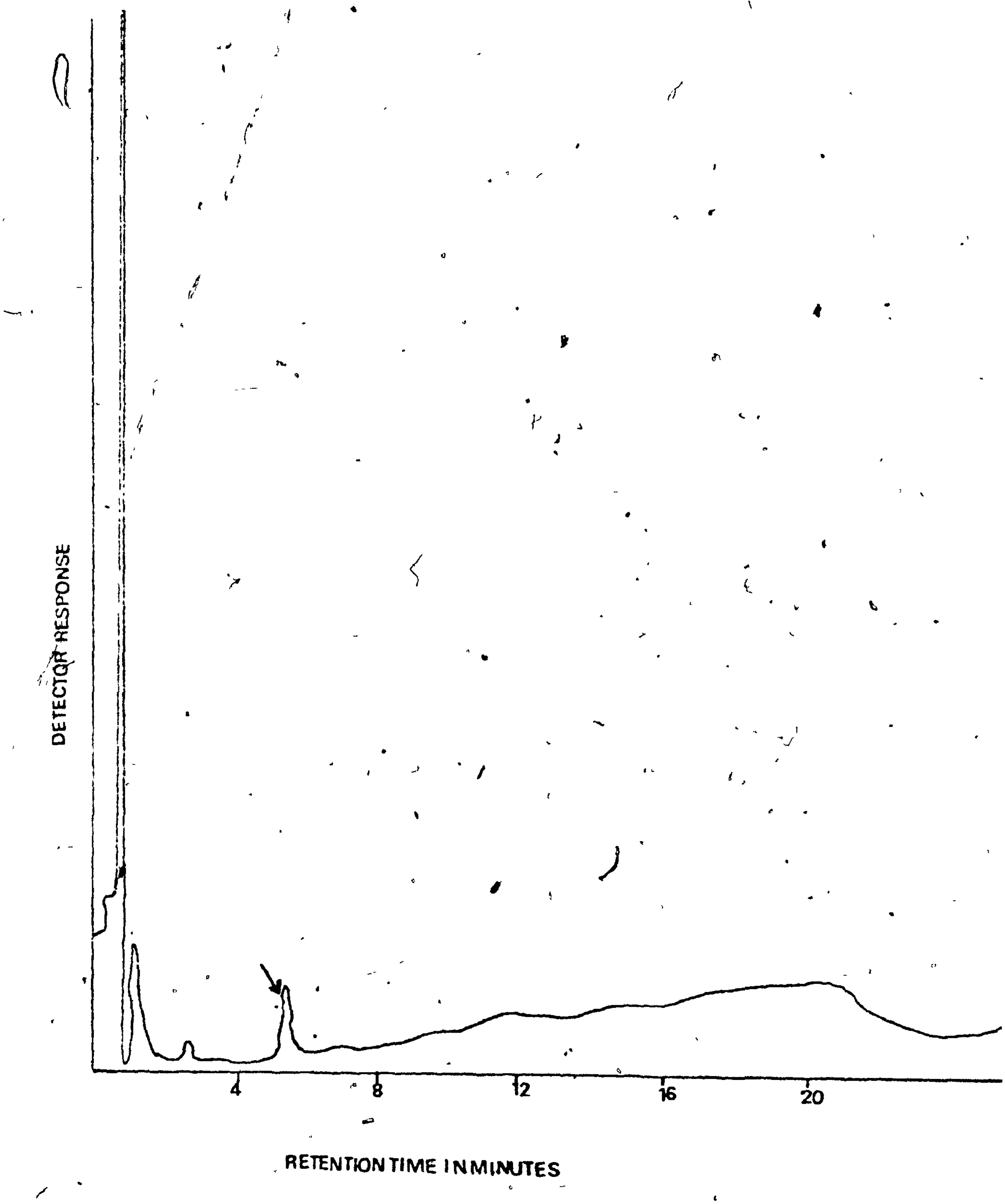


Figure 13. Soil residues - Recovery of Atrazine.
2C, 0-10", 4/8/71.

SOIL WATER AND SEDIMENT SAMPLING SITES 1972

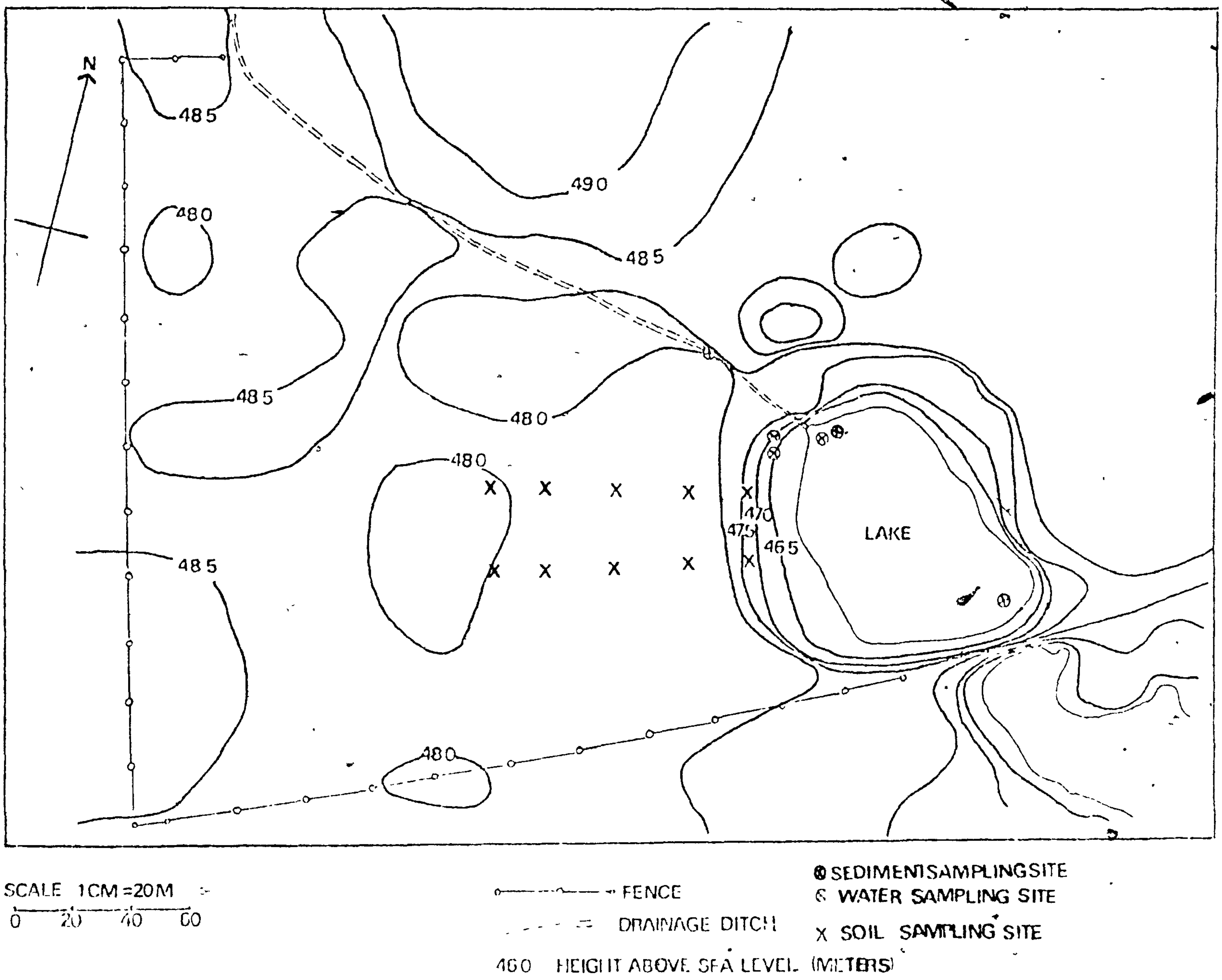


Figure 14. Soil, water and sediment sampling sites 1972..

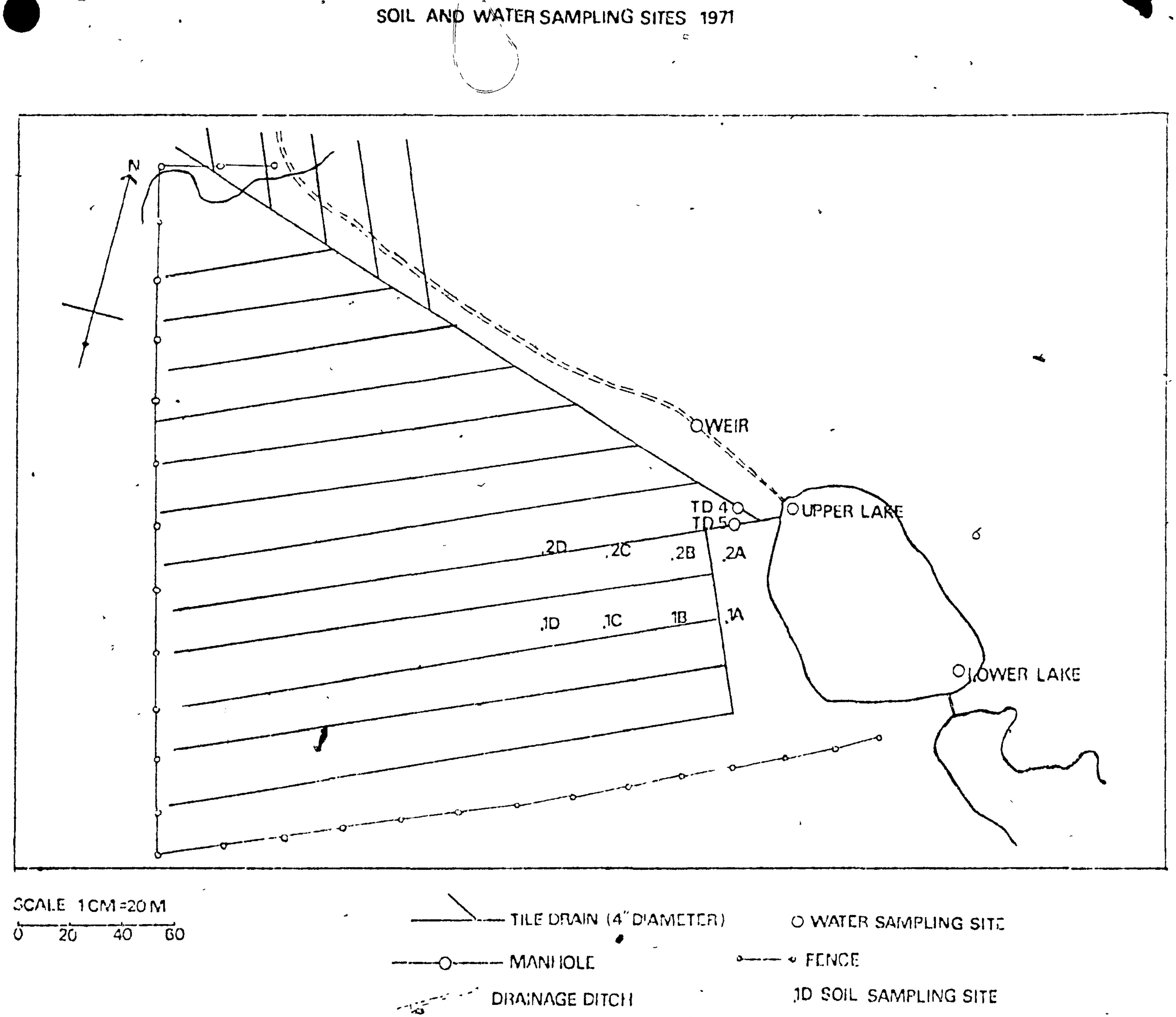


Figure 15. Soil and water sampling sites 1971.

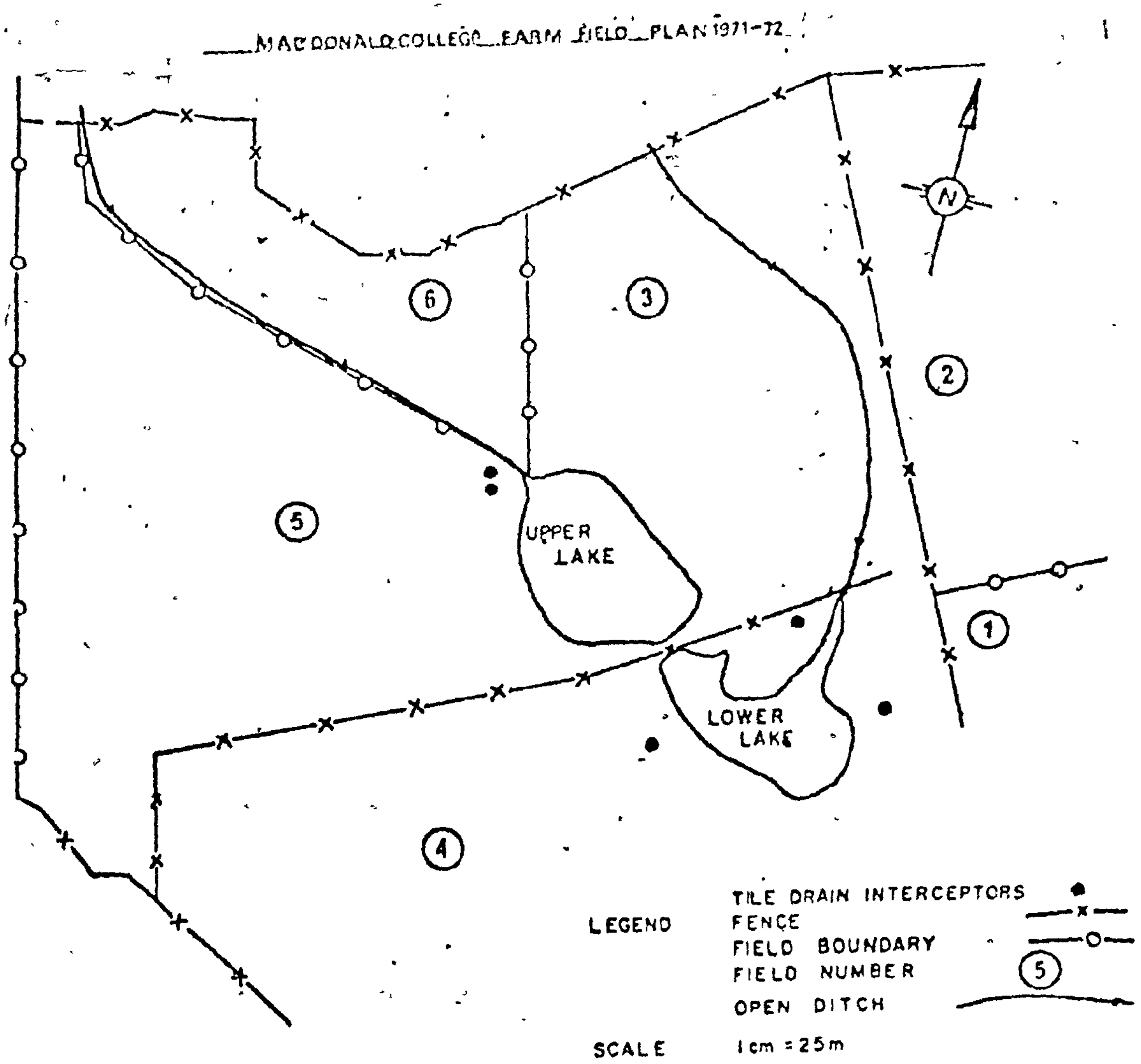


Figure 16. Macdonald College Farm field plan 1971-1972.