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Atrazine

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Atrazine

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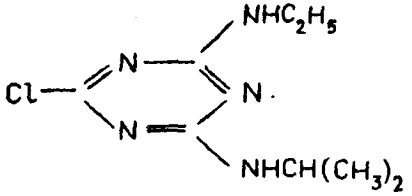
The series is intended for toxicologists, higienists and all those responsible for evaluation and control of harmful effects of chemicals to human health and the environment.

ATRAZINE

2-Chlor-4-ethylamino-6-isopropylamino-symm-triazine.
Atrazine is white, odourless crystalline substance [1,2].
Molecular formula.

$$C_8H_{14}ClN_5$$

Molecular weight 215.7
Structural formula.



Atrazine belongs to the group of herbicides which are derivatives of symmetrical triazines which are applied to destroy weeds in fields sown to maize, cotton and different stone fruit crops.

Synonyms: izaprim,G-30027, zeazine, primatol, hungazine PK[2], primatol A[3], atrazine, SOB, atratol 851 [4].

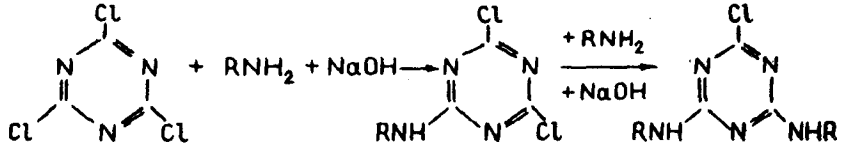
Melting point: 173-175°C[1,3,4,].
Relative vapour density.

Product vapour pressure at 30°C is approximately $4{:}10^{-5}$ P/3 10^{-7} mm Hg/ 1 , it is practically non-volatile.
33 mg atrazine are dissolved in I 1 [1]or 70 mg per I 1[3,6], 70 mg/1 are dissolved at T° = 27°C and 320 mg/1 – at 85°C (in chlorophorm – 52 g/1, in methanol – 18 g/1, in petroleum ether – 12 g/1, it is dissolved in gastric juice [4]).

PRODUCTION PROCESS

Triazines of the group 2-chlor-4-alkylamino-6-alkylamino-symm-triazines are obtained through interaction of corresponding amines with cyanurchloride

in the presence of inorganic or organic bases for bonding HCl. The reaction follows 2 stages:



Atrazine is received through a consecutive substitution of chlorine in cyanurchloride during the interaction with ethylamine and further on – with isopropylamine in the presence of alkali [1,3].

The compound is produced in the form of wettable powder containing 50% of the active ingredient, a filler and a surface active substance. Chalk or caoline is used as the filler [2, 4, 6]. Besides this, it is manufactured in paste form containing 30-40 of the active substance, mineral oil and supplementary substances [1]. Of late, triazine herbicides are used in the form of mixtures. For instance, the preparation having the name of agelon consists of 33.3% of atrazine and 16% of prometrine [6].

USE

Symm-triazine have found the greatest practical application as herbicides, dyes and for the production of plastics [3,6].

It is used to control weeds in maize (prior to the sowing, by embedding, concurrently with the sowing or prior to the sprouting of the crop), coriander (spraying of the soil before sprouting), in fruit crops and in grape vines (spraying of the soil before sprouting), in fruit crops and in grape vines (spraying of the soil in early spring prior to the sprouting of weeds or in the autumn after harvesting), in currant, gooseberry and raspberry (in early spring prior to the sprouting of weeds) for the Caucasian yam (prior to sprouting) [1].

Atrazine, just as other triazines and in a mixture with them, is applied to control the overgrowing of sewers [7].

Atrazine is effective against the following weeds: wild buckweed, field mustard, cocklebur, drug fumitory, chickweed, rag weed, field pennycress, and some other weeds; it is not active against wheat grass [1]. It is applied on the non-cultivated grassland as a total action herbicide. It is also used to control annual dicotyledonnous and weeds of the grassy family [8].

PATHWAYS INTO THE ENVIRONMENT

The main pathways into the environment are applications of the preparation into the soil and its subsequent penetration of the ground water.

The preparation is applied into soil as a solution and a solid. The rates of consumption vary: it is 1.5-4 kg/ha on maize fields [1], it may be 3-8 kg/ha [2,4] – prior to the sprouting of the crop, it is 1.5-2 kg/ha on the fields of

coriander [1], 3-4 kg/ha [2,4] – prior to the sprauting of the crop, it is 6-8 kg/ha in fruit crops [1], 4-12 kg/ha – in the spring, prior to the sprouting of weeds and 12-16 kg/ha – in the autumn when soil is sprayed [2,4], it is 2-6 kg/ha when treating currant, gooseberry and raspberry [1] etc.

The activity of the preparation is strongly influenced by the nature of soil. The rate of application is lower on sandy soils; the rate should be much higher on black soil and on other soils with a high humus content [1].

Atrazine is stable in soil and it is recommended to plant cultures resistant to this preparation even on the next year after the treatment [1].

Atrazine may be preserved in soil and ground water up to 1.5-2 years. Given an application rate of 12 kg/ha, it occurs after a passage of 428 days at a depth of 5-50-60 cm in volumes ranging from 0.2 to 0.1 mg/kg [4]. Complete decomposition of the preparation with a destruction of the molecule by soil microorganisms sets in after the passage of 18-20 months. The rate of decomposition depends upon the climate and primarily upon temperature [1].

The persistence of symm-triazines is greatly retarded in conditions which facilitate the development of microflora. In the subtropical climate of Adzharia triazines disappear completely from the plough layer in 110-120 days at an application rate of 5-20 kg/ha.

The minimum content of atrazine which influences the growth of susceptible crops is as follows: 0.05 mg/kg for sandy loam soil, 0.13 mg/kg for organic, 0.1 mg/kg – for loamy soil [9]. Convection plays the main role in the micromovement of symm-triazines in soil (the diffusion rate for atrazine is $15.2 \cdot 10^{-8}$ cm^2 (at 25°C) [9]. The rate of atrazine inactivation depends upon temperature, humidity, aeration and the type of soil. Decomposition of atrazine increases with temperature and humidity when aerobic conditions are replaced by unaerobic. The inactivation rate is particularly high at a temperature ranging from 40 to 60°C and humidity – 60 to 100%. A certain exception are the results of experiments with the soddy-podzolic subtropical and brown mountain–forest soils where inactivation of atrazine has one and the same rate in anaerobic and aerobic conditions [10].

The rate of atrazine movement along the soil profile is higher in the zone of humid subtropics than in the moderate humid conditions and it may be found at a depth of 50 cm after 5 months. Being identified with the passage of 8 months after application at a dose of 20 kg/ha atrazine was found at a depth of approximately 70 cm (during that period the rainfall was 1,322 mm and soil temperature was $\geqslant 15$°C). Under these conditions, thanks to the activity of the soil microflora, the herbicide being applied at a rate of 5 and 10 kg/ha was inactivated, the herbicide content was within 0.4 kg/ha. Detoxication was completed within 11 months. The maximum decomposition of atrazine was observed in the course of the last 3 months [11].

Reduction processes in soil facilitate more rapid inactivation of atrazine as compared to the oxidation processes.

In an experiment with a meadow-bog soil after the passage of three months since atrazine application it was found in a soil layer of 0-20 cm, being applied at larger rates (20 kg/ha) the herbicide reached down to 20 cm and when applied at smaller rates (5 kg/ha) – down to 10 cm. With the pas-

sage of 5 months in the mentioned experiment atrazine was inactivated almost completely [11]. The depth of penetration and the rate of detoxication was determined by the method of biological indication through the growing of sensitive culture on soil specimens taken from different depths in the experimental sections [11].

Leaching of atrazine along the profile of red soil is more intensive and reaches greater depth than is the case in the meadow-bog soil which is the result of a better water permeability of red soil. In its turn, notwithstanding the different intensity and depth of leaching of atrazine, its inactivation in the meadow-bog and red soils is of one and the same rate [12].

Detoxication of atrazine is also considerable owing to the high temperature of soil, specifically so in humid subtropics [12].

The particularly rapid loss of atrazine phytotoxicity is noted at humidity ranging from 50 to 100% of the complete moisture capacity in case of aerobic conditions and it ranges from 30 to 100% given anaerobic conditions.

The distinctions in atrazine detoxication are associated also with the conditions of soil aeration. Thus, given aerobic conditions in the specimens of meadow-bog and red soil treated with atrazine at a rate of 3.32 mg/kg all oats were killed whereas the reduction was only 80 and 75% in the same specimens given anaerobic conditions, which corresponds to the amount of the herbicide in the soil – 0.6 and 0.95 mg/kg, respectively. Similar changes have been noted in other soil types (soddy-podzolic in Moscow Region and the black soil (thick layer) in the Krasnodar territory) [12]. The authors associate the inactivation of the herbicide in soil with an increased activity of the anaerobic soil microflora and also, which is more important – with the physico-chemical and primarily with the reduction processes taking place in the soil in the absence of oxygen [12].

U. Ya. Spiridonov and V. I. Kamensky [10] associate the rate of atrazine inactivation with the type of soil and specifically with temperature and aeration. As for the ability to inactivate atrazine the authors list soil types in the following order: black soil > soddy-podzol subtropical, > soddy-podzol Moscow Region > black soil alpine-meadow, black soil carbonate, brown alpine-forest, meadow-bog > brown alpine-forest, chestnut. Acid soils possess somewhat greater activity as regards the inactivation of atrazine [10].

The majority of authors place atrazine with stable compounds. This question, however, is debatable. In some papers it is stated that soil herbicides which are applied in the autumn are completely washed out by July-August, that is when weeds develop particularly intensively, which is a proof of the absence of expediency of their application in the autumn, in the conditions of subtropics [11]. Other authors, in their turn, place atrazine with the preparations with a long period of action since at a rate of 3 kg/ha – the afteraction of the preparation in different soils persisted for 5-7 months, while applied at a rate of 10 kg/ha – 15 months [13].

The period of herbicidal action in the meadow-bog soil when symm-triazines are regularly applied is shortened. The main cause of the accelerated detoxication is most likely the adsorption of triazines by persisting species of weeds: Digitaria sanquinalis and Paspalum digitaria [14]. When symm-triazines

are in soil, they are subject to numerous chemical and biochemical transformations which lead to dehalogenation, N-dealkylation, hydrolysis of amide and ether bonds, the opening of cycles and (in anaerobic conditions) reduction of the nitrogroups [9].

CONCENTRATIONS

Atrazine represents a certain danger for animals since it has considerable persistence in soil and plants and also owing to its ability of accumulation in human organisms. Poisoning of farm animals with atrazine may take place when livestock grazes on treated areas prior to the expiration of the period necessary for herbicide decomposition; when animals are given fodder containing remains of herbicides at a rate which is higher than the maximum allowable concentration [4].

Atrazine arrives in plants from soil thorugh the root system; with the transpiration current it moves into the stalk, leaves and other organs of plants. With the passage of a short period of time it may be found in the surface parts of plants. The herbicide may also penetrate plants thourgh leaves. When an alcohol solution of atrazine (which is carbon labelled) was applied to leaves of 10-12 day old Suks variety beans, we observed limited arrival to other organs of the plant though it proceeded at a very low rate. When atrazine is introduced into the Knop nutritive media, i.e. when the herbicide comes through the root system, it was found in all parts of the bean plant, within several hours. With the passage of 5-6 days atrazine content in the surface part of the plant was so high that it led to the death of plants (at a concetration in the solution of 1.6 mg/l).

The analysis of data on the percentage distribution of atrazine in plants shows that given a 24 hour exposure more than 75% of the preparation which entered the plant was localized in the surface part, 42% – in leaves. With the increase in exposure to 2-5 days, atrazine content in roots dropped to 14-16% whereas the share of atrazine in leaves was 66-71% of the total content in the plant. When it was applied to leaves the entire labelled preparation was first found only in the treated leaves. With the increase in the period of exposure to the preparation the radioactivity of the treated leaves went down while that of the leaf stalk it increased sharply (approximately twice). Given a three-day exposure, up to 80% of the applied atrazine was localized in the treated leaf and in its stalk, in case of a 5 day exposure S up to 72.6%; the total amount of the herbicide localized in the other parts of the bean plant given a three or five day exposure was approximately the same comprising 13 and 12.2%, respectively [8]. Labelled atrazine was identified in plant organs by measuring radioactivity using a BFL-25T end-on counter. The transition of labelled atrazine from the nutritive medium into plants was identified by means of radioautography [8].

An experiment with young plants of maize and wheat grown on Pryanishnikov's nutritive medium with an addition of atrazine at a rate of 2

mg/l of the solution indicated the absence of atrazine in the first 3 hours of the experiment in maize roots and leaves. Wheat which is susceptible to atrazine in the same organs. Subsequently we observed a steady increase of atrazine in wheat leaves whereas the accumulation of atrazine in maize leaves was very small. [15]. Some authors believe that the indicated distinctions in the atrazine accumulation are associated with a rapid transformation of the herbicide in maize into other forms of the compound. Atrazine content in the organs of plants was determined by Gizin's and Knyusli's spectrophotometric techniques [15].

When sunflower was grown on a full mixture of Gelrigel with introduction of atrazine into the 9th leaf formation stage at a rate of 1 kg/ha, the herbicide was largely accumulated in the leaves of the upper and lower tiers, at the growth point and to a lesser degree – in stalks and roots. This regularity persisted both in the opening (4th day), and during the remote date of determination (7th day). Its content on the 9th day was approximately only 50%at the growth point and it increased in the leaves of both tiers.

To study atrazine distribution in cellular cultures of sunflower leaves the plant was grown on a sand culture with the application of Gelrigel mixture. Atrazine was applied in the 4th leaf formation stage. After the passage of 7 days following the application of the herbicide, atrazine was found in all the structural units of the cell (nuclei, chloroplasts, mitochondria, conductive tissue and the supranatal fluid) with the greatest accumulation in the supranatal fluid (rhibosomes, microsomes, plasma proteins) and in the fraction which is known as the conductive tissue [16].

The determination of atrazine was carried out by spectrophotometry using the Mayer-Delley technique: the plants were finely fragmented, and submerged in chlorophorm for atrazine extraction [16].

The study of atrazine content in the black soil and the grey podzolized soil after its application into the upper (10-15 cm) soil layer at a rate of 2-10 kg/ha has shown that on the day of application both soils contained one and the same amount of atrazine at the level of 1.15 ÷ 3.27 mkg/g of dry soil subject to the experiment variant (with plants or without) and subject to the amount of atrazine which was applied to the soil. Inactivation of atrazine in time (up to 4 months) occurs at one and the same rate in both soil types and its inactivation in the rhizosphere in both soil types was much more intensive than in the soil without plants. This was particularly pronounced in the phase of heading of panicles and flowering of maize. Thus, there was no difference between the amount of atrazine in the plant rhizosphere in the black soil without plants at the beginning of the experiment; in the second period it comprised 0.93 mkg/g, and subsequently 0.92 and 0.29 mkg/g. In the gray podzolized soil we found 0; 0.90; 0.45 and 0.37 mkg/g, respectively. These regularities were observed in the experiment variants with the application of atrazine at a rate of 10 and 2 kg/ha [17]. The determination of atrazine in the soil, in this case, was made by using a dried, granulated and sieved (d = 0.5 mm) soil. Atrazine extraction from 50 g of soil was carried out by chlorophorm, the extract was washed by a solution of NaOH and HCl, and then with distilled

water. The determination of atrazine was carried out by a modified technique of Meyer and Dalley [17].

In the meadow-bog soil of the Kobuleti district after the passage of 40 days since the application of atrazine at a rate of 5 kg/ha we found 3.05 kg/ha of the product; with the passage of 70 days – 1.4 kg/ha; with the passage of 110 days – 0, and at a rate of 10 kg/ha with the passage of 40 days – 6,2; with the passage of 70 days – 3.0; with the passage of 110 days – 0.32 kg/ha [10].

Observations conducted over many years (10-fold application of atrazine in soil) did not show a direct negative effect upon the microbiological and biochemical processes of the meadow-bog soil in the humid subtropics of West Georgia [18].

As it was shown previously, atrazine gradually migrates from the upper soil horizons into more deep lying layers and at a depth of about 30 cm from soil surface it is found in smaller volumes than at a depth of 60-120 cm. This leads to the contamination of water bodies and communal water systems which take their water both from surface water sources and from artesian water wells.

It has been shown by numerous studies that problems of residual atrazine in food products, do not arise, as a rule. When soil surface is treated 2-3 days prior to the sprouting of maize at a rate of 5-10 and 20 kg/ha for 5 years running, atrazine residues have not been found in maize grains [14, 19].

The determination of atrazine in the stalks and leaves of maize grown in three districts (Zaporozhye, Moscow Region and Stavropolye) at a rate of 1.25-3 kg/ha did not reveal its presence in any of the mentioned organs of the plant. An excess of atrazine dose up to 8 kg/ha was neither accompanied by the accumulation of the product in any of the examined specimens of maize. Experimental specimens of maize grown on the soil treated with high rates of atrazine (ranging from 3 to 8 kg/ha) were subjected to an organoleptic evaluation using the method of closed sampling. The results have shown that experimental specimens did not differ from the control by their organoleptic properties.

Residual amounts of the preparation have not been found in potatoes, peas, beans and black currant berries grown on the soil treated with atrazine. The mentioned studies help to make a conclusion about the absence of any counterindications from the point of view of hygiene against the application of atrazine as a herbicide for maize, patato, beans, peas and black currant plantations [20]. At the same time there are indications proving the worsening of the quality of products when atrazine is applied. Thus, given a 5-year application of atrazine at rates of 5, 10 and 20 kg/ha on meadow-bog soil of humid subtropics of West Georgia the harvest was not as high as expected and there was a lowering of the standard of grain of maize. This grain had a diminished content of nitrous protein, protein, fat, while protein had an increased amount of zein – a biologically inadequate fraction. No residue of atrazine was found in maize grain [19].

The following maximum allowable concentrations of atrazine have been fixed for food products in the USSR: 0.1 mg/kg in fruit and vegetables, 0.25 mg/kg in graincrops, 0.02 mg/kg in meat and eggs, 0 in milk [2, 4, 9].

ENVIRONMENTAL FATE TESTS

One of the factors of herbicide detoxication in soil is the activity of soil microorganisms which destroy herbicides and use them as nutritive substances. Thus the study of the application of triazines (symazine, atrazine, prometrine, propazine) as sources of nitrogen nutrition in the presence of biologically active substances indicated that fungi (Fugarium oxysporum, Penicillium adametzi Zaleski, Aspergillius versicolor Tirabaschi, Penicillium citrimum Thom, Penicillium cyclopium Weste Cladosporium Transchelli Pidopl et Daniak) use best of all prometrine and atrazine. Actinomycetes (Actoelicolor, Krassilnikov Actglobisporum Krassilnikov, Act flaveolus vas restur vas nov. Act fumosus Krassilnikov, Act globisporus var flavofuscus) make more intensive use of prometrine [21].

The high humidity and temperature in the upper layers of subtropical soils during 5-6 months of the vegetation period facilitate intensive decomposition of herbicides of root action by microflora [12].

The determination of atrazine toxicity by biological indication did not reveal any dead oats even in the upper layer (0-10 cm) of soil with the passage of 8 months after the application of the preparation at a rate of 20 kg/ha. The content of herbicide in that layer was 0.4 kg/ha. When atrazine was applied at a rate of 5 and 10 kg/ha there was complete inactivation of the preparation. The authors associate the indicated processes with the activity of the soil microflora [11].

Information on the influence of atrazine and of other symm-triazines on soil microflora is rather contradictive. Atrazine was applied at a rate of 1.3 and 5 kg/ha using a handpowered sprayer into soddy-podzolized, well-cultivated sandy-loam soil in spring. Subsequently, microflora was studied being taken from between the maize rows at a depth of 0-5, 5-10 and 10-15 cm. With the passage of 1 month after the application of the herbicide the amount of fungi went down to 51% as compared with the control; with the passage of 3 months the amount of fungi dropped 3-5 fold as compared with the control. After a year since the application of atrazine at rates of 1,3 and 5 kg/ha in soddy-meadow, sandy-loam soil the fungi flora was noticeably inhibited. There was no correlation between the dose of the herbicide and the degree of its action upon fungi. The authors suppose that in cultivated soils with a large content of organic substances and in soils of a heavier mechanical composition the negative action of herbicides upon soil microflora would be less owing to a more rapid detoxication of the herbicide as the result of its sorption by soil. As for the soils, which are poor in organic matter and are of a lighter mechanical composition, the herbicide toxicity would persist for a longer time which leads to the inhibition of the fungi flora.

It should be also noted that the application of herbicides influences differently different species of fugi. Thus, in soil with the predomination of fungi of the species of P. nigricous, P. purpurogenum, Fusarium sp, Trichoderma sp. there was not a single case of complete disappearance of these species. A noticeable reduction in the amount of fungi of P. nigricous (up to 2.9-7.4% compared with the control) was observed with the passage of

3 months after the application of the herbicides. One year after the application, the amount of fungi of this species increased as compared to the control, Fusarium sp. and Trichoderma proved to be resistant to triazines.

The alteration of the species composition of soil microflora when herbicides are applied occurs owing to the larger or smaller resistance of different species of fungi, which in its turn, is not stable and depends upon the properties of the soil, pH, the action of other soil microorganisms, etc.

The study of the growth of colonies of different species of fungi in pure cultures showed that Fusarium solani was particularly sensitive and the inhibition of its growth by 25-50% was observed already at a rate of 0.01 kg/ha. Fusarium moniliforme was retarded in its growth by 25-50% when atrazine was applied at a rate of 10 kg/ha. Particularly resistant was Penicillium janthinellum and Fusarium oxysporum whose inhibition in excess of 25% was observed only at a rate of 100 kg/ha. In a pure experiment all fungi experienced growth inhibition but the extent of this inhibition was subject to the rate of herbicide application [16].

The determination of fungi was carried out by the method of soil solution suggested by Suprun and Bekker, and with planting of soil suspension upon Chapec's medium. In laboratory conditions the fungi were applied by three injections into Chapec's medium with the addition of the herbicide. The planted dishes were incubated at a temperature of 25-27°C and the diameter of the grown colonies was measured with the passage of 5 days [22].

When the influence of herbicides upon the dynamics of the microbiological developments in a soddy-bog soil was studied we determined the strength of bacteria, fungi and oligonitrophiles after a 10-fold application of atrazine and subsequent thermostating. In this we did not observe any change in the activity of the nitrofying microorganisms. No considerable changes in the numerical strength of the microflora or of its activity was determined. The activity of soil microorganisms, most likely, is more associated with lack of purity of experimental plots than with the number of applications of the herbicide into the soil [18].

Thus, the inactivation of atrazine in soil is carried out by soil microflora and plants. The main part in detoxication of atrazine is played by microorganisms, since in the soil where plants were growing, approximately the same amounts of atrazine were found as compared with the soil without plants, where only the microflora could have influenced atrazine. The determination of atrazine was carried out by a modified method of spectrophotometry of Mayer and Dalley [17].

During the incubation of F. roseum with atrazine the latter was subjected to changes with the formation of an oxyderivative atrazine as the main metabolite [9].

The presence of a herbicidal effect which differs in different soils with symm-triazines and also the regularity of their decomposition in soil give grounds to believe that when the herbicide is introduced into soil there sets in a definite relationship between the fractions of the herbicide which are, in different extents, available for plants and microorganisms. With the assimilation of the fraction which is available to plants and microorganisms, part of

the herbicide changes from an unavailable state to an available one. The higher the assimilating capacity of soil, the greater is the part of the herbicide fixed by the soil to a state which is inaccessible for plants [23].

Photodegradation of atrazine in water, methanol, ethanol, H-butanol occurs when it is exposed to ultraviolet light with a wave length less than 300 nm. The maximum rate of transformation occurred at a wave length of 260 nm.

The photolysis of atrazine in water leads to the breaking away of chlorine to the 2-triazine ring and the formation of 2-oxi-triazine. In methanol the chlorine atom is substituted by a metoxygroup with the formation of atranon; in the ethyl and buthyl alcohol there takes place the formation of 2-etoxy and 2-butoxyderivatives. Atranon and its oxyanalogue are the final products of photolysis in the media where they are formed [9].

The processes of the hydrolysis of symm-triazine derivatives in soil are strongly influenced by pH and are rather weakly influenced by the presence of organic substances in the soil [9]. The rate of inactivation of atrazine depends upon soil acidity; acid soils possess a somewhat greater activity in relation to the decomposition of the herbicide [10].

There is no direct information concerning the hydrolysis of atrazine in soil. However, when the herbicidal activity of a combined preparation was determined (nitrofoska + atrazine) it was demonstrated that there is a loss of toxicity of triazines which was associated with the unfavourable influence of pulp acidity. The study was conducted in vegetation experiments with the application of combined preparations at a rate of 1 kg/ha atrazine. Besides this, a 50% wettable powder of atrazine was held for 15 days in solutions with pH being 0,1 and the HCl and 0.1 of NaOH. Then it was applied into soddy-podzolized soil limed by exchange acidity. The test-crop was spring wheat. The result of the experiment indicated a practically complete absence of herbicidal activity of the chloride and alkaline suspension of atrazine. The holding of atrazine at pH 2,4 and 11.1 had but slightly weakened the effectiveness of the preparation while holding it at pH = 7 did not affect its toxicity [24].

The effectiveness of herbicides was considerably influenced by soil adsorption properties. Defferent volumes of the herbicide which is available for plants remains in different soils. The greater is the adsorption of the herbicide by soil the longer its herbicidal effect.

Thus, during the study of the effectiveness of atrazine in different soils, good agreement was demonstrated of the indicators of the adsorbing complex of 4 types of soils (black soil, red soil, soddy-podzolized loam and gray soil) with the results of the mechanical analysis of soils and the content of the organic substance. A clear dependence of soil properties upon the effectiveness of the herbicide was demonstrated, namely: the greater the presence of the small fraction (< 0.001 mm) and of the organic substance in soil and the greater the adsorbing ability of the soil, the greater part of atrazine is fixed by soil to a state which in unaccessible for plants (with the exception of gray soil) [23].

The adsorption of symm-triazines by soil colloids influences strongly their technological effectiveness. Participating in this process are not only the organic substances of the soil but the clayey minerals too. The mechanisms of adsorption may change subject to the soil pH, adsorption may be also influenced by soil humidity, temperature, the composition of the soil solution [9].

Symmetrical triazines under vapour pressure exceeding $1 \cdot 10^{-6}$mm of the mercury column $1.33 \cdot 10^{-3}$ P) evaporate rather intensively at 20°C from systems with a neutral pH; compounds with vapour pressure below $0.3 \cdot 10^{-6}$mm of the mercury column ($4 \cdot 10^{-4}$P) are relatively not volatile at this temperature. Upon soil surface the volatile property of preparations drops sharply owing to adsorption. It increases with soil humidity [9]. The rate of inactivation of atrazine depends upon temperature, aeration and soil character. The loss of herbicidal activity sets in more rapidly at a temperature of 20-40°, 50 and 60° than at 20-40° or 10° [10].

BIOCONCENTRATION /CLEARANCE TIME/ MAMMALIAN METABOLITES

The questions of metabolism of symm-triazines both in plant organism and in warm blooded animals are still studied inadequately.

The absence of expressed characteristics of cumulation of the substance in the organism of test animals, and also the availability of information about the absence of atrazine or of its metabolites in a number of organs, milk and urine of mammals prove its rather rapid decomposition with the formation of poorly toxic products of metabolism. There is information that the rate of decomposition of atrazine in the organism of warm-blooded animals is quite high. Thus, even after an acute exposure of animals, atrazine in its unaltered form was practically not found in blood or in organs and excreta of animals immediately after exposure [25]. No residue of the preparation was found in internal organs including the uterus, placenta and skeletal muscles of large-horned cattle which received atrazine with fodder for 48 days at a rate of 1 and 30 mg/kg of fodder (the sensitivity of the method was 0.1 mg/kg) [4]. The milk of cows which were exposed to atrazine for 21 days at a dose of 3,15 and 100 mg/kg in fodder, did not show any atrazine or oxiatrazine on the second and on the seventh day after the termination of exposure while the method sensitivity was 0.04-0.05 mg/kg. Multiple exposure of cows to atrazine at a rate of 5 mg/kg, atrazine was found, on the first day of the preparation's arrival at a rate of 0.03 mg/kg and then on the fourth day – at a rate of 0.12 mg/kg, in the urine of the test animals. Following two days after the termination of feeding animals with atrazine, the urine of test animals did not show any amount of the preparation [4].

Desalkylation is the most important mechanism of transformation of triazines in animal organisms [2].

In the organism of animals, just as in plants, the main direction of the metabolism of 2-chlor-symm-triazines is the formation of conjugates with glutathion, with the final product of decomposition – mercapturic acid [9].

The organism of rats and other mammals exhibits the processes of N-dealkylation and also (though in a smaller degree), the co-oxidation of N-alkyl lateral chains. Thus, alongside the metabolite of atrazine which has been completely dealkylated, we find in the urine of rats and rabbits small amounts of N-(2-chlor-4-amino-symm-triazinyl-6) glycine and N-(2-chlor-4-amino-symm-triazinyle-6) alanine. It is believed that in the organism of animals the hydrolysis of 2-chlor-symm-triazines takes place but with great difficulty.

The reaction of decomposition of symm-triazines is accompanied with the formation of products which are less dangerous for animals than the initial compounds [9].

MAMMALIAN TOXICITY ARRAY

The toxicity of atrazine was studied in different species of animals and birds (mice, rats, rabbits, dogs, sheep, neat cattle, chicken, wild ducks etc) under different pathways of its arrival in the organism and also given different duration of exposure (acute, subacute and chronic experiments). Thus, the average nonlethal dose of atrazine when administered into the stomach of albino mice is 1.42 g/kg [3], 0.85 ÷ 1.57 g/kg [2], 1750 mg/kg [9], 1500 mg/kg [20], when administered in the stomach of albino rats – 2.17 g/kg [3, 20], 3080 mg/kg [9], 1.41÷3.33 g/kg [2]. DL_{50} for rabbits is 600 mg/kg [4]. According to the results of studies by A. V. Kovalenko [5, 26, 27], the average lethal dose of atrazine for albino mice and albino rats calculated after the method of Miller and Teitner is 850 ± 157 mg/kg and 1410 ± 333 mg/kg (respectively) in terms of pure substance. There are also the values of average nonlethal doses for laboratory animals which equal 1400÷3300 mg/kg [1].

The toxic dose for sheep was 250 mg/kg. When atrazine was given daily at a rate of 50 mg/kg the sheep perished following 199 days after the beginning of the action of the preparation, at a dose of 100 mg/kg sheep died after 16 exposures and at a dose of 400 mg/kg – after 2 exposures. Quaile die on the 7th day following daily exposure to atrazine at a rate of 5760 mg/kg in fodder. Six day old wild ducks die on the 5th day after daily exposure to atrazine at a rate of 19560 mg/kg in fodder [4]. When being given with food for five days, atrazine's DL_{50} for quaile is 5766 mg/kg, it is 19560 mg/kg for wild ducks [9]. Atrazine rates of 100 mg/kg and 1600 mg/kg are toxic on the strength of morphological characteristic.

The lethal dose for sheep is 400 mg/kg; heifers die after a double administering of atrazine per os at a dose of 250 mg/kg. The average lethal dose for chicken is 2,200 mg/kg [4]. The DL_{50} for wild ducks exceeds 2 g/kg [9].

There are also indications about partial perish of laboratory animals when they were given atrazine per os. Thus, when atrazine was given to albino rats at a dose of 1 g/kg two animals out of 20 died. The remaining rats showed clear symptoms of intoxication: sluggishness, untidy appearance, intensified diuresis, salivation [28]. The comparison of the values of DL_{50} of hime-made and imported preparations demonstrated greater toxicity of the home-made specimen [26].

Thus, given an acute effect of atrazine we observe clear species distinctions in sensitivity; sheep and neat cattle are particularly sensitive to this herbicide.

The acute lethal poisoning in case of inhalation of atrazine was not observed [29, 2, 5]. The administering of the herbicide at a concentration of 1.15 ÷ 1.17 mg/l for 40 minutes did not lead to the death of any of the 7 rats which were exposed to the preparation. However, we did observe hemotological biochemical and pathomorphological changes one month after the exposure [5]. The mentioned concentrations of atrazine (1.15÷1.17 mg/l), on the first day after the exposure induced an increased sugar content and an alteration of the protein composition of the blood serum with an increase in the amount of total protein, a decrease in the albumine fractions and an increase of the globuline fraction at the expense of the α-fraction. The restoration of the disturbed functions back to normal was observed only with the passage of two weeks after the termination of the exposure [30].

In case of a daily two-hour exposure by inhalation for a month at a concentration of atrazine ranging from 0.1 to 0.9 mg/l we observed a symptomocomplex, which proved the damaging but not a lethal effect [29]. Atrazine concentration of 0.05 mg/l is regarded as a threshold value in an experiment with a single exposure [29].

The clinical picture of an acute lethal poisoning of test animals when they were given symm-triazines (atrazine, symmazine, ipazine and chlorazine) is of one and the same type and is characterized by sluggishness, adynamia with subsequent brief periods of motoric excitation, breathing insufficiency, nose bleeding. Considerable diuresis has also been noted. Onset of death, subject to the dose, was within the first hour, 24 hours, two, three days and the latest – on the fourth day with the symptoms of adynamia and weakening of breathing [5]. The survived animals manifested an alteration of the protein spectrum of blood serum, an increased sugar content, of the lactic and the pyruvic acids in it, a liver disfunction, an inhibition of the function of the thyroid gland [3].

Information regarding atrazine resorption through the unlesioned skin is contradictive. There are indications about the value of the average lethal dose in case of atrazine skin application which proved to be 7500 mg/kg in experiments with rabbits [4]. The general resorptive action when atrazine is applied to skin at a dose of 1000 mg/kg is expressed but weakly [2]. When this substance is applied to skin at a dose of 0.5 g/kg and 1 g/kg we observed a change in protein forming, carbon function of the liver and the activity of the redox enzymes – catalase and peroxidase [30].

When atrazine was applied to the skin of a rat's tail – DL_{50}>1000 mg/kg [27]. Alongside with this there is information indicating the absence of the resorptive-toxic effect of atrazine when it is applied to the skin of rabbits, albino rats and mice [5, 29].

In case of a repeated administration of atrazine to the stomach of albino rats at a dose equalling 1/4 DL_{50}, 1/8 DL_{50}, 1/14 DL_{50} and 1/40 DL_{50} only some test animals died from the first two dosages [5]. In case of a repeated administration of atrazine at a dose of 1/10 DL_{50} to laboratory animals the coefficient of cumulation was more than 5 [2]. At the same time there is information proving a sufficiently pronounced extent of atrazine cumulation

the organism of test animals. Thus, the cumulation coefficient during the administration of the preparation to the stomach at dosages of 1/10-1/5 DL_{50} was 1.65-1.85 [4, 29] and even 0.2 [26], respectively.

Under the chronic supply of atrazine for 2 years with the feed at a dose of 15 and 150 mg/kg no symptoms of poisoning were indentified in dogs. The dose of 1500 mg/kg in the same conditions of the experiment produced a clinically pronounced intoxication in dogs [4].

Atrazine concentration of 0.018 mg/l is indicated as the threshold of a chronic action through inhaling [4]. Chronic (for 4 months) action through inhaling of atrazine at concentrations of the order of thousandth fractions of a milligram per litre induced weakly pronounced changes in the carbon and protein metabolism only in the third month of exposure to the preparation. As for the disturbances of the anti-toxic function of the liver they were not detected [31].

Under a six month action (administration into the stomach) of atrazine at doses of 0.1, 2 and 20 mg/kg we observed (in rats) clear symptoms of intoxication accompanied with the development of aggressiveness and death of some of the animals, with well pronounced intoxication and paralysis of the hind extremities. When a dose of 0.1 mg/kg of atrazine was administered, we noted increased permeability of blood vessels measured by means of a radioactive isotope (I^{131}), by 40% in the liver, 104% in the stomach, 48% in the heart, 22% in lungs, 24% in kidneys and 17% in the brain. At the same time when atrazine was administered at a dose of 20 mg/kg we observed a tendency to a decrease of the vascular-tissue permeability, i.e. an increase in the dose leads to a sharp diminishing of the inclusion of the isotope in the liver, lungs, stomach, heart, kidneys and the brain [32].

A dose of atrazine of 0.1 mg/kg, in a chronic introduction into the stomach is regarded as threshold considering its toxic effect [33].

The examination of the peculiarities in atrazine action upon some metabolic indicators and upon the functional state of liver was carried out in conditions of a single, repeated and chronic experiment when the substance was administered into the stomach and during the action through inhaling. Thus, in an acute and minimally lethal level of action (introduction into the stomach at a dose of 1 g/kg) there were changes in the protein composition of the blood serum with a decrease in the content of albumines and in an increase in globulines at the expense of the α-and β-globuline fraction. The content of total protein in this did not differ from the initial value. Within ten days since the administration of the preparation the decrease in albumines was observed in a greater degree as compared with the first examination while the increase in globuline fractions occurred at the expense of α-and β-globulines. One month after the experiment we observed a restoration of all the altered indicators [29, 31, 28, 34, 35].

The study of carbon metabolism in the same animals and in similar periods of time has shown no alteration of blood sugar – after 48 hours; a decrease in its level after 10 days and an increase – with the passage of 1 month. These changes consisted in shifts in time of glycemic curves after a galactose load with an even hyperglycemic coefficient. The glycogen reserves of the liver (a